

Great Smoky Mountains National Park

2010 Water Quality Annual Report



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GRSM 2010 WQ Annual Report

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This report describes for water quality monitoring and research activities in the Great Smoky Mountains National Park for calendar year (CY) 2010 work accomplished under a cooperative agreement between the U.S. National Park Service, Southeast Region and the University of Tennessee (Knoxville) under the Southern Appalachian Cooperative Ecosystem Studies Unit, **CESU Host Cooperative Agreement No. H5000095041**, task agreement Order No. J5471090010. University of Tennessee identifies task agreement as Research Account No. R01-1334-213.

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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 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.

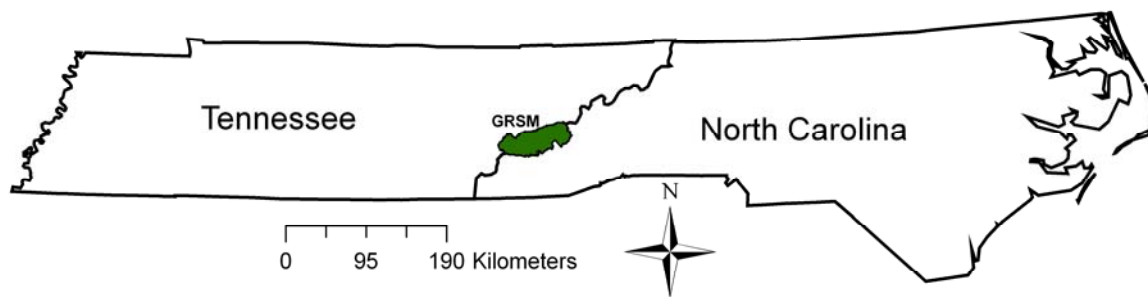


Figure 1-1. Location of Great Smoky Mountains National Park.

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 et al. 2009).

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.* 2009). 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 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 A).

1.1 Noland Divide Watershed

Noland Divide watershed (NDW) was selected for long-term monitoring following its use as a 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 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,

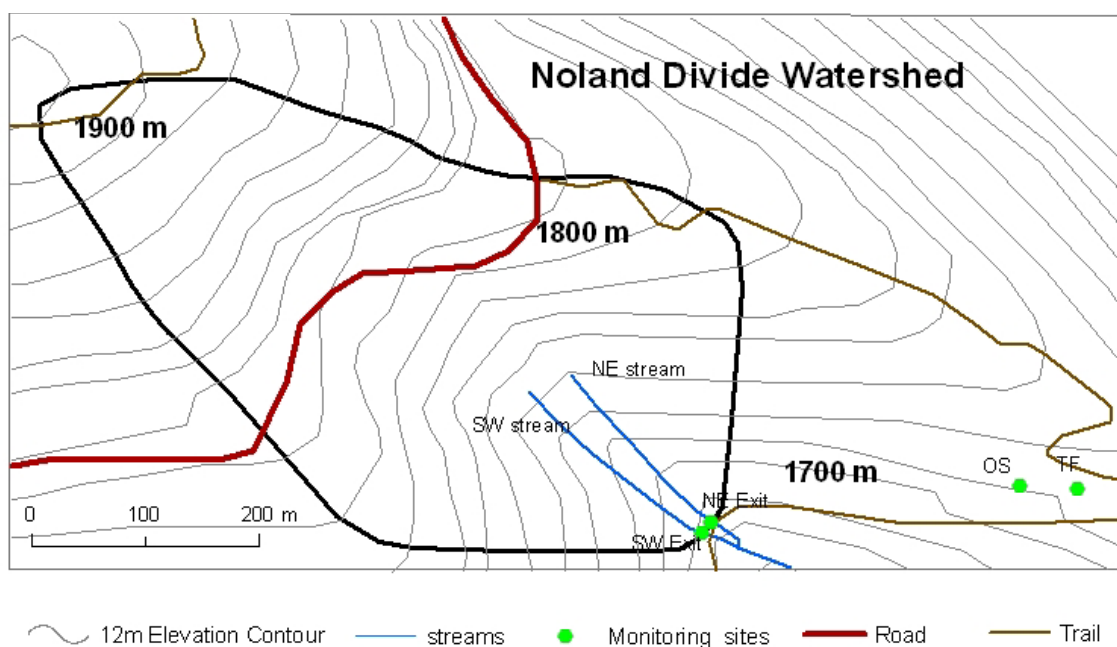


Figure 1-2. Map of Noland Divide watershed showing water quality monitoring sites.

yellowish-brown loam, a 20+ cm thick C horizon of olive-brown, loamy sand, and underlying 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



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

LDPE liners are used only to collect precipitation. The collected water samples from OS and TF sites 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). 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 recorded every 15 minutes and data is downloaded every two weeks with a YSI650® handheld device. 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, 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 acidic 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 (Odom 2003). 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).

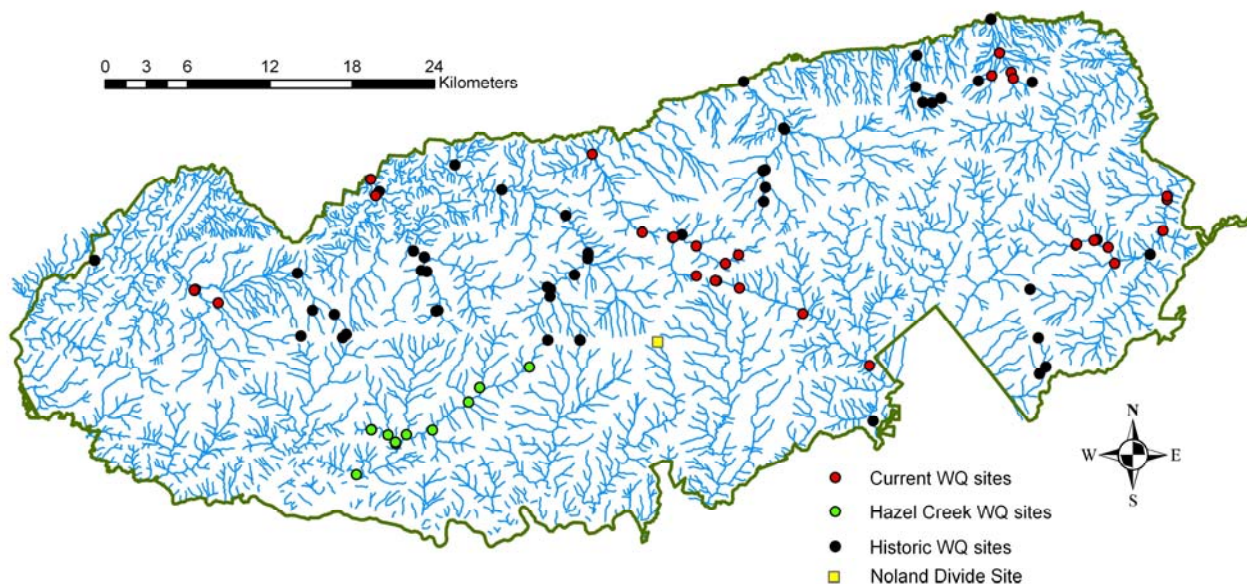


Figure 1-5. Water quality monitoring sites for the GRSM Park-wide survey.

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 by Neff *et al.* (2010) 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. 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. The following articles have been recently published since 2009 or are in progress for publication submittal:

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*. DOI 10.1007/s11270-010-0727-z.

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) in press.

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. DOI 10.1107/s00244-008-9269-4.

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.

Articles/Manuscripts in Progress for Publication:

Cai, M., A.M. Johnson, J.S. Schwartz, S.E. Moore, and M.A. Kulp. (*revisions submitted*). Soil acid-base chemistry of a high-elevation watershed in the Great Smoky Mountains National Park watershed affected by long-term acid deposition. . *Water, Air and Soil Pollution*.

Mauney, J.L., J.S. Schwartz, K.J. Neff, R.B. Robinson, S.E. Moore, and M.A. Kulp. (*in preparation*). Stochastically characterizing ecological impacts of episodic stream acidification. *Water Resources Research*.

Grell, M.E., J.S. Schwartz, A.M. Johnson, Cai, M., S.E. Moore, and M.A. Kulp. (*in preparation*). Relations between soil chemistry characteristics and basin factors in Great Smoky Mountains watersheds. *Catena*.

Neff, K.J., J.S. Schwartz, R.B. Robinson, S.E. Moore, M.A. Kulp, and T.B. Henry. (*in preparation*). Stream Episodic Acidification Response Based on Basin Factors in Great Smoky Mountains Watersheds. *Environmental Pollution*.

Zimmerman, G.T, M. Cai, J.S. Schwartz, K.J. Neff, S.E. Moore, and M.A. Kulp. (*in preparation*). Baseflow-stormflow comparisons of ion mass transport for streams in the Great Smoky Mountains National Park. *Hydrological Processes*.

2.0 Noland Divide Watershed: 2010 Data Summary and Discussion

2.1 Annual Precipitation Volume

The annual rainfall amount collected during 2010 was 195 cm, 18 cm below the 19-year average for this site (Figure 2-1). However, Only 176 cm TF precipitation was collected during 2010. This amount is 45 cm below the 19-year average, and 19 cm below the open site rainfall for this site. This low throughfall precipitation amount was slightly affected by the overflow of water in the collection bucket at the sample date of Dec. 21, 2010. The real TF precipitation should be slightly greater than 176 cm.

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

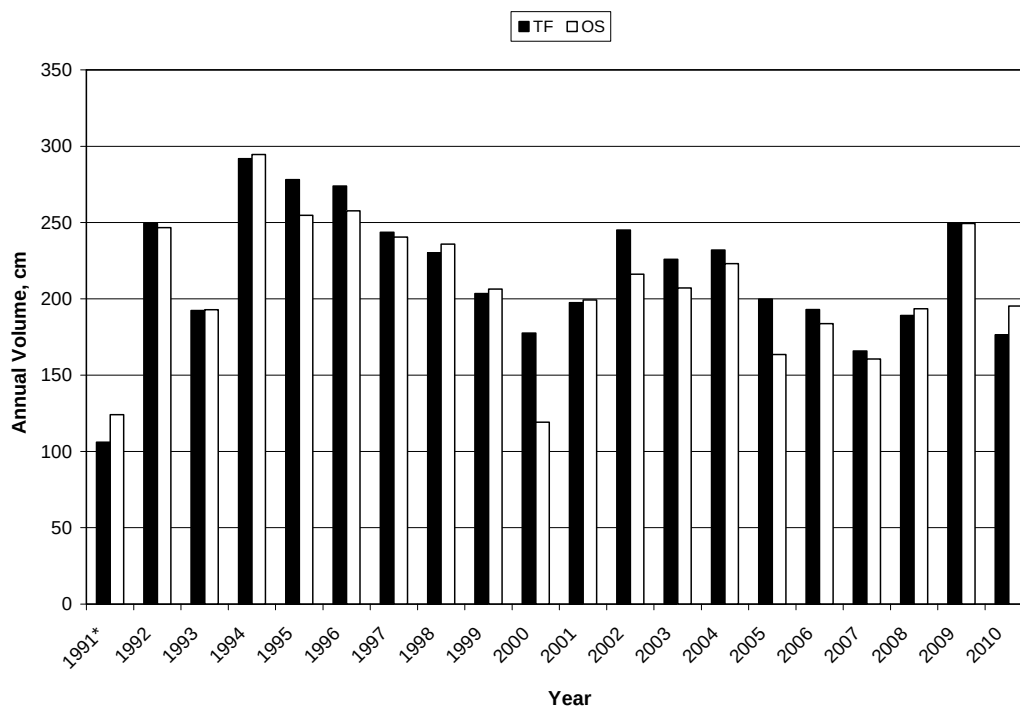


Figure 2-1. Total annual wet-only and throughfall precipitation volumes received by the NDW. acidification. Data for other anions/cations, and metal concentrations can be found in NPSTORET.

During 2010, the estimated amount of total inorganic nitrogen entering the NDW from wet-only (OS) precipitation was 145.59 equivalents of nitrogen per hectare per year (N eq/ha/yr) and from throughfall was 635.20 N eq/ha/yr (Figure 2-2). In 2010, wet-only OS deposition was 325 eq/ha/yr *below* the long-term 19-year average, and the throughfall deposition rate was 508 eq/ha/yr *below* the 19-year average. The especially low OS inorganic nitrogen deposition could be partially attributed to incomplete record in 2010. At the end of 2010 since November 11, the water sample was not able to be collected for chemistry analysis because of the frozen water in collection carboy. As a result, the chemical fluxes since November 11 was not counted in the total deposition fluxes for open site. Besides the reduction of nitrogen fluxes in open site caused by incomplete record, inorganic deposition by rainfall and throughfall may be actually reduced in 2010 since the difference to the

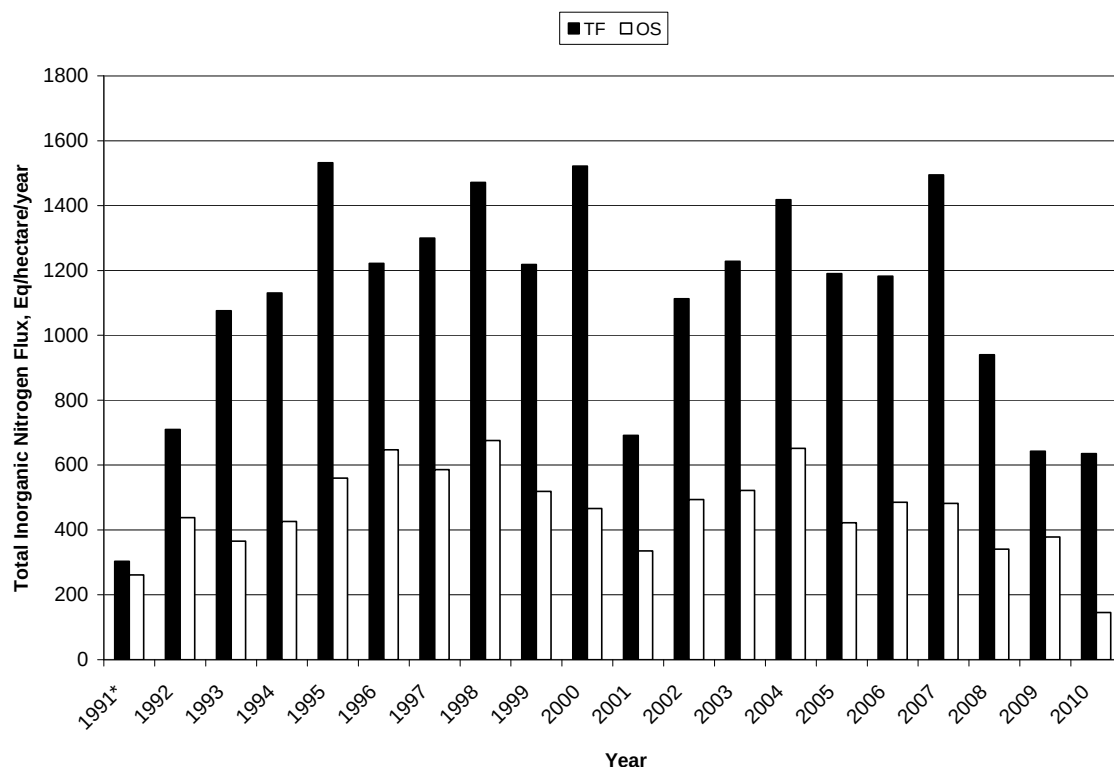


Figure 2-2. Total annual inorganic nitrogen deposition entering the NDW as wet-only and throughfall precipitation.

long-term 19-year average are so significant.

The estimated amount of sulfate entering the NDW from wet-only precipitation was 292.99 eq/ha/yr and throughfall was 561.45 eq/ha/yr (Figure 2-3). Sulfate deposition exhibited significant reduction as the deposition amounts from both throughfall and open site were only half of the amounts in 2009. Compared with the 19-year average, wet-only deposition was approximately 259 eq/ha/yr *below* the average, and throughfall deposition was 1137 eq/ha/yr *below* the average. The 2010 dry deposition rate for sulfate was estimated as 268 eq/ha/yr. 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). In 2010 significant reduction for sulfate and total inorganic nitrogen deposition fluxes were observed from the previous year, with totals below all other years of record (Figures 2-2 & 2.3). The significant decrease of acid anions deposition

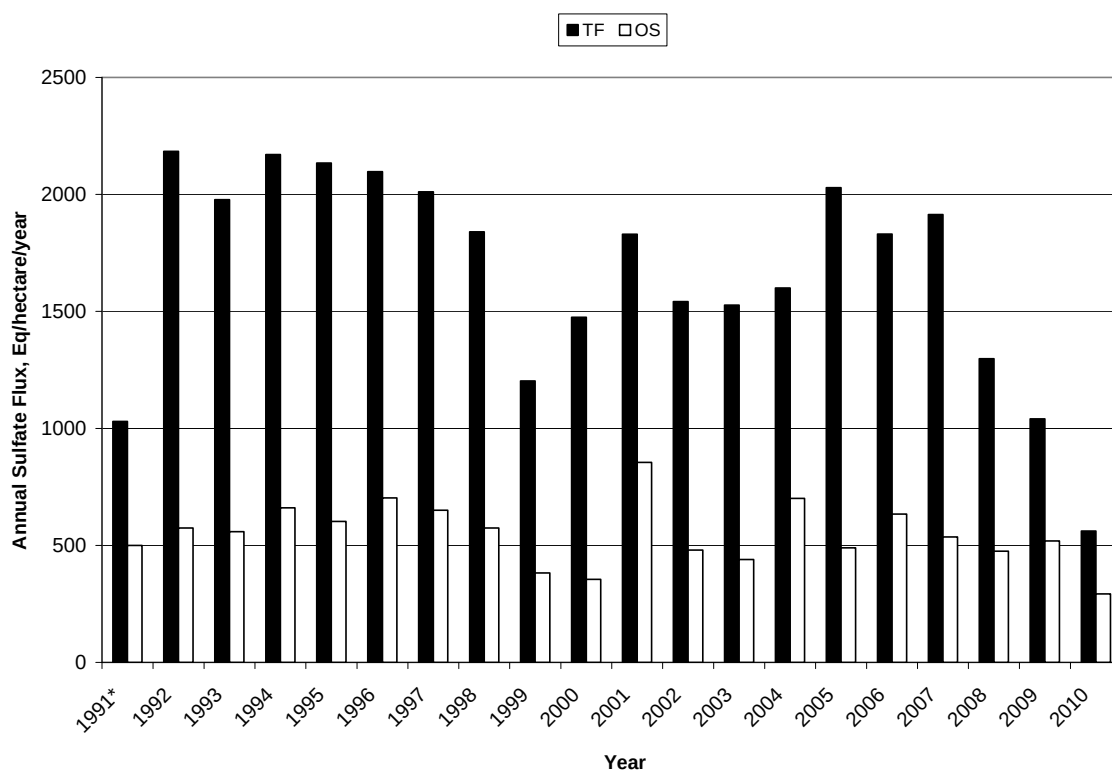


Figure 2-3. Total sulfate entering the NDW as throughfall and wet-only precipitation.

* 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.

resulted in the significant increase of throughfall pH. In 2010, throughfall pH was 5.24, 0.94 pH unit higher than the 19-year average (4.30). Compared to the average throughfall pH in 2009, it was elevated from 4.78 in 2009 to 5.24 in 2010. In contrast, no significant increase of wet-only precipitation pH was observed between 2009 and 2010. Compared to the 19-year average, the wet-only deposition pH in 2010 was 5.55, 0.77 pH unit above the average. The 2008 Annual Report recognized this observation as a result of recent emission controls of SO₂ and NO_x at coal-fired power plants west of GRSM, or possibly a function of the prolonged drought at that time.

A statistical analysis of the 17-year NDW data has been completed (1991-2007), and two manuscripts have been published (see pages 8 and 9). Cai *et al.* (2010) focused on a watershed mass balance of chemical inputs and outputs, and Cai *et al.* (2011) focused on long-term temporal trends and seasonal patterns. A third paper on the differences in mass transport between baseflow and stormflow periods has been prepared and will be submitted to *Hydrological Processes* in 2011.

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 2,098 mL, 2,060 mL, and 3,550 mL, respectively. However, volumes cannot be directly compared because of differential lysimeter efficiencies. Statistical summaries of the soil water chemistry for 2010 are in Tables 2-1, 2-2, and 2-3, which include pH/conductivity, anions, and cations, respectively.

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

		pH	Conductivity, $\mu\text{S}/\text{cm}^2$
Upper Lysimeter	2010 Min - Max	4.04 – 4.27	34.70 – 71.60
	2010 Average	4.17	49.37
	1991-2009 Average	4.04	64.06
Middle Lysimeter	2010 Min - Max	4.23 – 4.55	25.20 – 51.00
	2010 Average	4.40	33.22
	1991-2009 Average	4.37	39.93
Lower Lysimeter	2010 Min - Max	4.43 – 4.54	28.00 – 31.30
	2010 Average	4.49	29.27
	1991-2009 Average	4.48	33.66

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	2010 Min - Max	1.61 – 29.86	6.69 – 138.90	5.98 – 135.08
	2010 Average	16.77	72.30	67.43
	1991-2009 Average	28.13	136.41	92.63
Middle Lysimeter	2010 Min - Max	9.92 – 38.19	17.57 – 224.50	49.72 – 132.73
	2010 Average	20.11	67.28	95.94
	1991-2009 Average	27.95	73.63	100.15
Lower Lysimeter	2010 Min - Max	8.10 – 29.12	31.32 – 87.49	28.67 – 133.98
	2010 Average	14.13	56.16	86.81
	1991-2009 Average	23.66	81.10	91.38

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	2010 Min - Max	18.78 – 23.61	9.39 – 15.25	31.79 – 55.15	59.14 – 77.51
	2010 Average	20.88	12.01	42.45	65.69
	1991-2009 Average	26.59	22.50	27.17	51.79
Middle Lysimeter	2010 Min - Max	2.81 – 27.90	5.57 – 9.07	1.52 – 36.23	20.48 – 35.96
	2010 Average	17.54	7.04	18.58	30.96
	1991-2009 Average	23.42	10.60	20.76	26.13
Lower Lysimeter	2010 Min - Max	7.10 – 11.68	6.66 – 47.95	14.65 – 21.10	20.70 – 46.85
	2010 Average	9.57	22.95	17.98	32.51
	1991-2009 Average	19.90	9.44	23.82	37.59

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 (Cai *et al.*, *in press*).

Anion chemistry analysis (Table 2-2) found a decrease in chlorine, nitrate, and sulfate averages for 2010 compared to 19-year averages. Chlorine concentrations for upper, middle, and lower horizons decreased 11.36 $\mu\text{eq/L}$, 7.84 $\mu\text{eq/L}$, and 9.53 $\mu\text{eq/L}$, respectively. Nitrate concentrations for upper, middle, and lower horizons decreased 64.11 $\mu\text{eq/L}$, 6.35 $\mu\text{eq/L}$, and 24.94 $\mu\text{eq/L}$, respectively. Sulfate concentrations for upper, middle, and lower horizons decreased 25.2 $\mu\text{eq/L}$, 4.21 $\mu\text{eq/L}$, and 4.57 $\mu\text{eq/L}$, respectively. The significant reduction of nitrate and sulfate concentrations in upper soil horizon could be explained by the relatively low deposition fluxes of nitrate and sulfate in 2010. If nitrification is reduced by lower nitrogen deposition and drier soils, soil pH will increase and thereby create a soil condition for sulfate desorption. This observation suggests that the recent reduction in sulfate and nitrate deposition may be changing the soil water chemistry.

The base cation chemistry in 2010 varied greatly from the 1991-2009 average, especially in the upper soil horizons (Table 2-3). This large variance was probably because only several soil solution samples, 3 samples in upper layer, 6 samples in middle layer and 3 samples in lower layer, were collected in 2010. With such few samples, large variance cannot be avoided. Two manuscripts on NDW soil water chemistry are in review in the *Water, Air and Soil Pollution* and in press in the *Journal of Environmental Engineering* from in-situ and laboratory experiments (see Page 9).

Comparing the 2010 averages for soil water pH (4.17 upper A horizon, 4.40 middle Bw horizon, and 4.49 lower Cb horizon) to the 1991-2009 long-term averages, the pH increased significantly in the upper soil horizon while remaining relatively constant for the middle and lower soil horizons

(Table 2-1). This may be explained in part by the observed increase in rainfall and throughfall pH, which would increase proton transport in the uppermost soil horizon before the lower horizons. In addition, a reduction in deposition inorganic nitrogen would also create the environmental condition to increase soil water pH in the upper horizon by reducing nitrification rates. The multiple possible biogeochemical processes involved with soil water chemistry can only be interpreted with long-term monitoring data. Changes in the deeper soils appear to be more dependent on hydrological pathways and heterogeneity of the physical soil matrix (Cai *et al.*, *in press*).

2.4 Stream Water Chemistry

Stream water quality is monitored at the SW and NE streamlets biweekly (Table 2-4). Data for 2010 found average pH levels in the SW and NE streamlets to be 5.94 and 5.72, respectively. It appears pH has increased in the SW and NE streamlets from the long-term average (1991-2009) of 5.84 and 5.59, respectively. Stream sulfate levels were greater in 2010 compared to the long-term average 1991-2009. Sulfate in the SW and NE streamlets were 33.48 µeq/L and 44.49 µeq/L for 2010 compared to 29.90 µeq/L and 41.14 µeq/L for the long-term averages, respectively. In contrast, nitrate and calcium levels were less in 2010 compared to the long-term average 1991-2009. Nitrate in the SW and NE streamlets were 24.96 µeq/L and 30.25 µeq/L for 2010 compared to 40.35 µeq/L and 45.70 µeq/L for the long-term averages, respectively. Calcium in the SW and NE streamlets were 43.52 µeq/L and 52.10 µeq/L for 2010 compared to 46.66 µeq/L and 51.20 µeq/L for the long-term averages, respectively.

Increased sulfate levels should lower the stream pH rather than increase it as observed. However, nitrate levels were less in 2010 compared to the long-term average prior to 2010, suggesting nitrogen deposition and soil dynamics may now be having a greater influence on stream pH than in the past when sulfate deposition dominated. Stream pH levels are a function of both cation and anion

atmospheric deposition, biogeochemical processes in the soil, and the supply of acid pollutants from deposition and soil.

Table 2-4. Summary of 2010 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
pH	5.94	5.72
Conductivity	13.99	12.47
ANC	8.40	5.35
Cl	10.61	15.20
SO ₄	33.48	44.49
NO ₃ -N	24.96	30.25
NH ₄ -N	1.84	2.54
Na	21.69	23.32
K	7.93	11.16
Mg	16.48	21.03
Ca	43.52	52.10
Al	0.07	0.11

3.0 Park-wide Stream Survey

The Park-wide stream survey dataset for 2010 includes 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 May and August. As described in Section 1.2, Park-wide surveys for stream water quality began in GRSM in October 1993 with 367 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, 2010 WQ data are summarized from the 43 current sites. In addition throughout the following text, comparisons will be made between the 2010 data and previous data collected from October 1993 through November 2009.

3.1 Water Chemistry Results

Descriptive statistics of the WQ constituents for the 1993 to 2009 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 2010 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 4.80 to 7.50, and did not vary to any great extent (CV = 0.074). However, ANC was found to vary widely ranging from -14.831 $\mu\text{eq/L}$ to 1025.44 $\mu\text{eq/L}$ (CV = 2.01), likely due to differences in surficial geology, soils, seasons, and flow stage. The ANC values above 100 $\mu\text{eq/L}$ were from streams located in the Abrams Creek watershed, an area of the Park with carbonaceous limestone geology. Additionally, road construction impacts from the Cades Cove Loop repaving project in 2010 contributed to higher ANC,

conductivity,

Table 3-1. Descriptive statistic of 1993-2009 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	7.502	6.387	0.470	0.074
Median ANC (µeq/L)	-14.831	1025.440	97.714	195.984	2.006
Median Conductivity (µS/cm)	10.610	98.050	20.175	17.320	0.858
Median Chloride (µeq/L)	9.890	19.888	14.190	2.010	0.142
Median Nitrate (µeq/L)	0.000	57.141	19.534	16.180	0.828
Median Sulfate (µeq/L)	14.933	317.378	46.561	51.398	1.104
Median Sodium (µeq/L)	17.995	67.053	38.905	9.613	0.247
Median Ammonium (µeq/L)	0.000	0.000	0.000	0.000	0.000
Median Potassium (µeq/L)	3.772	15.745	10.784	2.877	0.267
Median Magnesium (µeq/L)	16.251	188.686	41.122	36.774	0.894
Median Calcium (µeq/L)	32.154	798.393	97.259	153.946	1.583
Median Aluminum (ppm)	0.015	0.434	0.045	0.065	1.435
Median Copper (ppm)	0.000	0.050	0.001	0.008	6.021
Median Iron (ppm)	0.002	0.030	0.015	0.007	0.455
Median Manganese (ppm)	0.000	0.283	0.008	0.043	5.377
Median Silicon (ppm)	1.339	4.510	2.760	0.706	0.256
Median Zinc (ppm)	0.000	0.156	0.011	0.028	2.586

pH, and base cations at sites 173, 174, and 489 during and following construction. In March, construction prohibited collection of Abrams Creek water quality samples. Like ANC, sulfate and calcium were found to be highly variable ranging from 14.933 µeq/L to 383.994 µeq/L (CV = 1.104), and 32.154 µeq/L to 798.393 µeq/L (CV = 1.583) respectively. 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 2010 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 2010 medians and the average of 1993-2009 site medians. Most ion constituents for 2010 were less than 10% different than the 17-year average. Higher percent differences between current and historical medians of dissolved metals and ammonium result from historically very low concentrations. Interestingly, nitrate was nearly 22% higher in 2010 possible because of increases in ammonia deposition. Nitrate has significantly increased over this period in many of the streams.

Table 3-2. Descriptive statistics of 2010 median water quality values for the 43 Park-wide stream survey sites.

Water Quality Parameter	Minimum	Maximum	Mean	Std. Deviation	*Percent Difference
Median pH	4.755	7.770	6.500	0.530	1.767
Median ANC (µeq/L)	-13.968	932.313	101.809	185.880	4.191
Median Conductivity (µS/cm)	9.265	108.800	20.804	19.257	3.115
Median Chloride (µeq/L)	5.002	19.689	12.873	3.024	-9.277
Median Nitrate (µeq/L)	3.685	61.082	23.794	17.487	21.805
Median Sulfate (µeq/L)	16.503	309.345	47.520	48.980	2.060
Median Sodium (µeq/L)	18.263	62.047	37.428	8.904	-3.798
Median Ammonium (µeq/L)	0.000	3.218	0.902	0.671	—
Median Potassium (µeq/L)	0.000	16.716	10.498	3.199	-2.651
Median Magnesium (µeq/L)	16.514	197.234	42.940	37.752	4.422
Median Calcium (µeq/L)	23.661	845.085	102.181	155.958	5.061
Median Aluminum (ppm)	0.000	0.445	0.054	0.069	18.406
Median Copper (ppm)	0.000	0.104	0.002	0.016	88.981
Median Iron (ppm)	0.008	0.182	0.039	0.031	156.100
Median Manganese (ppm)	0.000	0.203	0.007	0.031	-16.876
Median Silicon (ppm)	1.355	4.611	2.845	0.713	3.059
Median Zinc (ppm)	0.000	0.167	0.008	0.026	-22.420

***Percent Difference = (2010 average – 1993-2009 average)/(1993-2009 average) ×100%.**

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 C). WQ results for all samples are reported and archived in the NPSTORET database, however data quality is reported in this report. In 2010, 482 water samples were analyzed: i.) Stream Survey grab samples (n = 252); ii.) Noland Divide Watershed grab, open-site precipitation, lysimeter, and throughfall water samples (n = 80), and iii) soil water experiment water samples (n = 150).

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 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). The IC is fully automated, sending results to a computer with Dionex™ software in which computed concentrations are reported 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, with results for USGS standard checks 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., NH_4^+ in replicates, Table 4-1). Concentration differences were actually very small, near instrument detection limits.

Table 4-1. IC QA\QC for the anions/cations in 2010.

QA\QC Procedure	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+
Detection limits (DL, ppm)	0.03	0.03	0.01	0.003
Blank	<DL	not detected	not detected	< DL
Absolute average value in % difference in replicates	1.43% (n = 126)	3.58% (n = 126)	2.05% (n = 126)	13.32% (n = 42)
Average recovery in %	100.90% (n = 16)	99.74% (n = 16)	99.58% (n = 16)	99.44% (n = 15)

Table 4-2. IC QA/QC sample checks using USGS standard solutions for 2010.

Sample	Constituent	Number	USGS (ppm)	Avg. results (ppm)	% difference
N97	NH ₄ ⁺	128	0.296	0.298	0.64
N101	NH ₄ ⁺	127	0.463	0.443	4.32
N102	NO ₃ ⁻	175	3.470	3.240	-6.65
P51	Cl ⁻	174	1.24	1.21	-2.32
	SO ₄ ²⁻	174	1.99	1.98	-0.45

4.2 Inductively Coupled Plasma-Atomic Emission Spectrometry QA/QC(ICP-AES) Procedures

Major cations (Na, K, Mg, Ca) and six trace metals (Al, Cu, Fe, Mn, Si, Zn) were analyzed on the ICP-AES. To ensure acquisition of high quality data, several ICP-AES QA/QC procedures were performed during measurement of metals in the water samples from 2010. Standards were prepared using certified ICP reagents and deionized (DI) water. The 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 9 samples to ensure accuracy throughout the sequence. The results for the QCC samples are presented in Table 4-3.

A USGS trace metal sample was acquired to verify low concentration ICP-AES results and run every 9 samples. The most probable values were obtained from the USGS Standard Reference (<http://bqs.usgs.gov/srs/>) and compared to our ICP-AES results. The results are presented in Table 4-4 (note: USGS T-183 copper concentration is below instrument detection limit).

Table 4-3. ICP-AES quality control check sample results (n = 65).

Element	Mean (ppm)	Actual (ppm)	% Error *	Relative STDEV **
Aluminum	0.4987	0.50	0.27 %	3.07 %
Calcium	1.0131	1.00	1.31 %	6.54 %
Copper	0.5025	0.50	0.50 %	1.90 %
Iron	0.5098	0.50	1.96 %	2.76 %
Potassium	0.9720	1.00	2.80 %	6.38 %
Magnesium	0.9977	1.00	0.23 %	6.06 %
Manganese	0.5089	0.50	1.77 %	1.69 %
Sodium	0.4854	0.50	2.93 %	4.09 %
Silicon	1.0107	1.00	1.07 %	2.53 %
Zinc	0.4928	0.50	1.45 %	3.42 %

* 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 = 58).

Element	Mean (ppm)	Actual (ppm)	% Error*	Relative STDEV**
Aluminum	0.1283	0.127	0.99 %	5.20 %
Calcium	11.3921	11.6	1.79 %	4.86 %
Copper	0.0030	0.0036	16.24 %	115.66 %
Iron	0.2060	0.206	0.01 %	1.96 %
Potassium	2.7163	2.57	5.69 %	4.71 %
Magnesium	7.7718	7.89	1.50 %	2.48 %
Manganese	0.0498	0.0492	1.30 %	3.16 %
Sodium	12.9842	12.7	2.24 %	3.85 %
Silicon	3.8780	3.87	0.21 %	2.85 %
Zinc	0.0859	0.0864	0.60 %	8.92 %

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.

Table 4-5. ICP-AES Blank (deionized water) sample results (n = 49).

Element	Mean Value (ppm)
Aluminum	-0.0019
Calcium	-0.0669
Copper	-0.0004
Iron	0.0017
Potassium	0.0176
Magnesium	0.0053
Manganese	0.0001
Sodium	-0.0075
Silicon	-0.0012
Zinc	-0.0005

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 analyzed 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.

Table 4-6. ICP-AES replicate sample results (n = 13).

Element	Median Absolute Percent Difference	n
Aluminum	37.81 %	10
Calcium	7.35 %	12
Copper	—	0
Iron	57.84 %	8
Potassium	3.62 %	9
Magnesium	1.14 %	13
Manganese	5.91 %	8
Sodium	4.94 %	12
Silicon	1.06 %	12
Zinc	12.48 %	4

Table 4-7. ICP-AES spike sample results (n = 16).

Element	Average Percent Recovery
Aluminum	100.53 %
Calcium	102.25 %
Copper	102.71 %
Iron	102.56 %
Potassium	98.52 %
Magnesium	99.05 %
Manganese	102.90 %
Sodium	101.81 %
Silicon	101.05 %
Zinc	103.33 %

Table 4-8. 2010 ICP-AES detection limits.

Element	2010 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

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.

QA/QC were good with two out of a total 252 samples for the Park-wide stream survey exceeding an ion balance $\pm 15\%$. For the NDW samples, 29 samples out of a total of 80 samples fell out of the $\pm 15\%$ range. 13 of these samples are throughfall samples and have ion difference from -16.55% to -45.45%. High organic acid concentration in throughfall samples was found to contribute the negative ion difference. Ten of these samples are soil water samples and have ion difference from 17.94% to 53.17%. The positive ion difference may be attributed to high aluminum concentration in

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	-6.45 %	-7.67 %	-7.71 %	-25.35 %
Absolute % Ion balance	7.64 %	8.62 %	13.44 %	25.35 %

soil solutions. Ion balances for NDW SW and NE streams, open sites and throughfall are summarized in Table 4-9.

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. The University of Tennessee Water Quality Lab generally only 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.

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	MPV1	UT-results	Z-value	% difference
T-199	Al	0.0916	0.081	-1.91	-11.57%
	Ca	3.80	3.70	-0.50	-2.63%
	Cu	0.0018	0.00198	-0.82	-9.09%
	Fe	0.169	0.171	-0.21	-1.17%
	K	1.76	1.87	-0.99	-5.88%
	Mg	6.36	6.20	0.51	2.58%
	Mn	0.015	0.0141	1.21	6.38%
	Na	7.66	7.72	-.21	-0.78%
	SiO ₂	5.39	5.46	-0.26	-1.28%
	Zn	0.0082	0.00623	2.63	31.62%
P-49	Conductivity	8.55	10	-0.66	-14.50%
	pH	6.49	6.70	-0.87	-2.94%
	Cl	1.04	1.05	-0.27	-0.95%
	SO ₄	0.34	0.418	-1.90	-18.66%
	Mg	0.33	0.34	-0.36	-2.94
	Ca	0.73	0.741	-0.19	-1.48%
	K	0.11	0.08	1.36	37.50
	Na	0.34	0.321	0.58	5.92%
N-103	NO ₃ ⁻ as N	0.320	0.3092	-	-3.34%
	NH ₄ ⁺ as N	0.270	0.2683	-	-0.74%

1 Most Probable Value

2 Misreported as 3.09 mg/L – decimal error.

3 Misreported as 2.68 mg/L – decimal error

5.0 References

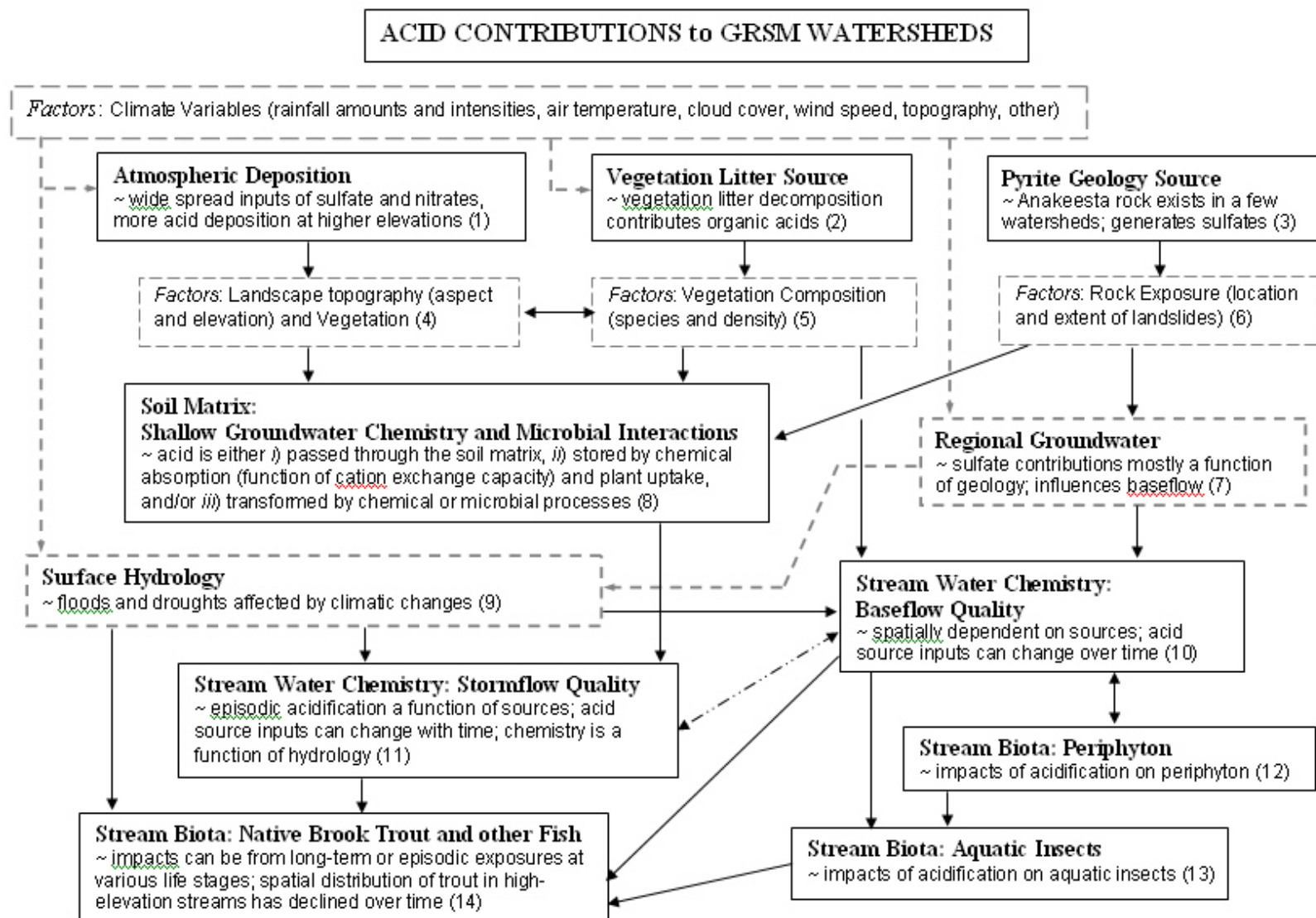
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APPENDICES

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).