



Great Smoky Mountains National Park 2014 Water Quality Annual Report

Natural Resource Report NPS/GRSM/NRR—2016/1130



Noland Divide
Open Site Rainfall

ON THE COVER

Noland Divide Watershed Study Site

Photograph by: Keil Neff, University of Tennessee, Knoxville, August 2005.

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February 2016

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

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Please cite this publication as:

Schwartz, J. S., M. Gonzalez, A. Veeneman, and M. A. Kulp. 2016. Great Smoky Mountains National Park 2014 water quality annual report. Natural Resource Report NPS/GRSM/NRR—2016/1130. National Park Service, Fort Collins, Colorado.

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Executive Summary

The Great Smoky Mountains (GRSM) National Park Annual Water Quality (WQ) Monitoring Program consists of: 1) detailed hydrologic and WQ monitoring at Noland Divide Watershed (NDW), a high-elevation forested site, and 2) Park-wide stream survey monitoring. This report summarizes all available data collected for the GRSM monitoring program, from 1991 through 2014. In 2014, volumes of precipitation collected at the throughfall site (TF) and the open-site collection station (OS) were equivalent to 209 cm and 79 cm, respectively. The mean pH of precipitation samples collected at the TF and OS sites was 5.40 and 5.01, respectively. Precipitation pH at these two sites has been trending upward since 2007; prior to that year pH remained below 4.4 and 4.0 at TF and OS, respectively. Annual sulfate deposition loads at NDW in post-2008 years (< 700 eq/ha/yr) have been consistently less than in pre-2008 years ($> 1,100$ eq/ha/yr). In 2014, TF sulfate deposition was 681 eq/ha/yr, or 32.7 kg-SO₄/ha/yr. Reduction in sulfate deposition likely is the result of reductions in sulfur emissions from regional coal-fired power plants, two of which are within 100 miles of the GRSM. The 2014 TF data indicated a continuation of a generally decreasing trend in total inorganic nitrogen (T.I.N.) deposition since 2008. In 2014, TF T.I.N. deposition was 896 eq/ha/yr, or 40.6 kg/ha/yr. Since 2008, the proportion of deposited T.I.N. consisting of ammonium has increased. In 2014, soil water pH in all soil horizons was higher than prior year measurements. Mean concentrations of chemical constituents in soil water were generally lower in 2014 than the overall mean concentrations over prior years. The NDW NE and SW streamlets had an annual average pH of 5.72 and 5.94, and an annual average acid neutralizing capacity (ANC) of 10.0 and 17.7 $\mu\text{eq/L}$, respectively. Of the Park-wide stream survey sites monitored in 2014, 13 of the 241 samples had a pH of less than 5.5, and four samples had a pH less than 5. A total of 114 stream survey samples ($\sim 47\%$) had pH greater than 6.0. Concentrations of potentially toxic soluble aluminum ≥ 0.2 mg/L (an important biological-effects threshold concentration) included four of the 241 samples analyzed in 2014. Aluminum was below the analytical quantitation limit (0.1 mg/L) in nearly 93% of the stream survey samples. Samples with aluminum concentrations greater than the biological-effects threshold for aluminum occur at locations of low stream water pH, consistent with dissolution of aluminum minerals in soils and bedrock. The overall mean pH was 6.05 for the Park-wide streams monitored in 2014. It is apparent that each GRSM watershed has a unique combination of factors (i.e., bedrock geology, soil, and vegetation) that influences biogeochemical processes, and thus the fate of acid pollutants entering, and transported through, GRSM watersheds. Park-wide data from both monitoring programs provide critical information to assess aquatic resource health. It also supports BGC-Pn-ET model calibration and verification for estimating critical acid deposition loads, and predicting possible recovery trends.

Acknowledgments

Monitoring was 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. H5000095040, Task Agreement Order No. J5471090012. The University of Tennessee identifies task agreement as Research Account No. R01-3601-194. We thank the volunteer support of Trout Unlimited for the bimonthly Park-wide water sample collections, and the University of Tennessee students' volunteer time supporting research activities.

List of Terms, Small Glossary, Acronyms, or Contacts

ANC	Acid Neutralizing Capacity
BDL	Below Instrument Detection Limit
CEE	Department of Civil and Environmental Engineering
CV	Coefficient of Variation
DI	Deionized Water
eq/ha/yr	Equivalents per hectare per year
GRSM	Great Smoky Mountain National Park
IC	ion chromatograph or ion chromatography
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectrometry
N	Nitrogen
NADP	National Atmospheric Deposition Program
NDW	Noland Divide Watershed
NPSTORET	National Park Storage and Retrieval
OS	Open Site (<i>Noland Divide Study Site</i>)
QA/QC	Quality Assurance / Quality Control
QCC	Quality Control Check
T.I.N.	Total Inorganic Nitrogen
TF	Throughfall (<i>Noland Divide Study Site</i>)
UTK	University of Tennessee - Knoxville
WQ	Water Quality

1.0 Introduction

Since the 1980s, national air quality monitoring has shown that the Great Smoky Mountain National Park (GRSM) receives elevated levels of acid pollutants from atmospheric deposition sufficient to cause stream acidification (Shubzda et al. 1995; NADP 2009; Sullivan et al. 2007; Silsbee and Larson 1982; Cai et al. 2011a, 2012). Acid pollutants originate from emissions of combustion by-products from sources such as regional coal-fired power plants, in addition to vehicular exhaust (Chestnut and Mills 2005; Stachurski and Zimka 2002; Stoddard 1994; Weathers et al. 2006). Commonly observed in the eastern United States, high elevation watersheds with naturally base-poor cation buffering capacity tend to be most vulnerable to the effects of acid deposition (Hyer et al. 1995; Driscoll et al. 2001). Most streams in the GRSM are low in acid neutralizing capacity (ANC), and very susceptible to chronic and episodic acidification (Robinson et al. 2008; Deyton et al. 2008; Neff et al. 2013). Low-ANC streams affected by acidification can transport high concentrations of aluminum and other acid-cations, released from weathered soil minerals. Such conditions adversely affect aquatic organisms in those streams. When soil water pH drops below 5, soluble monomeric aluminum (Al_{IM}) can be released entering nearby streams, and Al_{IM} can be toxic to aquatic biota (Baldigo and Murdoch 1997; Neff et al. 2009). Based on initial studies in the 1980s linking stream water quality and atmospheric acid deposition, the GRSM initiated a long-term continuous water quality (WQ) monitoring program in the early 1990s to investigate and monitor conditions within the GRSM. The current GRSM WQ program includes: 1) detailed hydrologic and WQ monitoring at Noland Divide (a high-elevation forested watershed); and 2) the Park-wide stream survey designed to characterize water quality under base-flow conditions. In this report, data are summarized for 2014, and compared with prior years' data to identify long-term trends in WQ parameters.

2.0 Noland Divide Watershed

Noland Divide watershed (NDW) was selected as a part of the long-term water quality-monitoring program in 1991 after completion of the Integrated Forest Study. The Integrated Forest Study was an American and European program to study acid rain effects on forest nutrient cycling, in which the NDW was one of several sites studied (Johnson and Lindberg 1992; Lindberg and Lovett 1992). Ongoing monitoring at NDW continues to assess effects of stream acidification by better understanding the biogeochemical processes as deposited acid pollutants are transported by water from forest cover into the soils and then to streams. In addition, NDW data are used in the calibration of the BGC Pn-ET Model which will predict future conditions for various acid deposition scenarios and estimate critical loads for the GRSM (Zhou et al. 2011).

2.1 Introduction

NDW is located in the GRSM about a half-mile from 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 1,680 m to 1,920 m (Figure 1). Two adjacent first-order streams originate from this watershed (NE and SW streamlets) and merge to form Noland Creek. 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

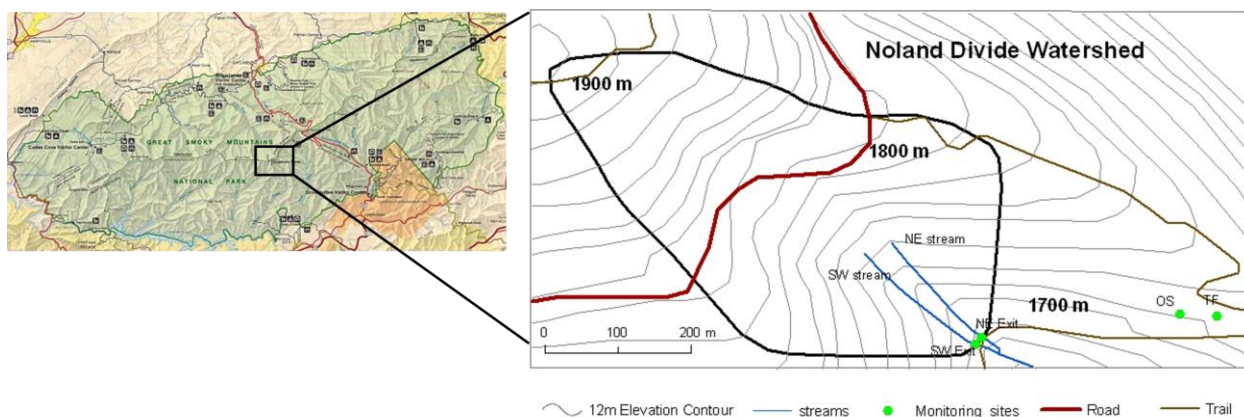


Figure 1. Map of Noland Divide watershed showing water quality monitoring stations (OS = open site, TF = throughfall site, SW and NE = streamlet sites). Soil lysimeters are installed within the TF site.

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). In the 1990s, 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 organic 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 sandstone bedrock. Underneath the soil is massive thick-bedded and low porosity Thunderhead sandstone, composed of quartz and potassic feldspar (King et al. 1968).

2.2 Study Activities and Methods

Five NDW hydrological stations were installed to monitor the potential effects of long-term acid deposition (Figure 1). These stations include: wet precipitation (open site, OS), throughfall (TF), soil water from lysimeters, and two streamlets (southeast, SE; and northeast, NE sites). This monitoring design provides a means to assess impacts from acidic deposition, both wet and dry deposition (OS, TF sites), effects of soil biogeochemical processes on pollutant fate and transport, and stream acidification response based on levels of atmospheric acid inputs to the watershed.

OS and TF samples are collected every two weeks except during extreme winter weather. Wet-only precipitation is collected at the OS site free of tree cover/canopy. Sampling atmospheric deposition in 2014 was accomplished with an ADS00-120 Sampler (N-CON Systems, Inc., Georgia). TF is collected at an "under tree canopy" site, located at the same elevation. During winter operations starting in December, TF is collected at two collection sites situated 50 m apart, within an electric fenced area to protect against wildlife vandalism. During summer operations, TF is collected using nine buckets dispersed throughout the same area. OS and TF samples are collected in 5-gallon

plastic buckets, which are weighed prior to being subsampled into 250-mL plastic bottles. Precipitation volumes collected since the previous collection date are estimated based on the measured field weight and the area of the bucket or funnel opening, and converted to centimeters of water depth per hectare (cm/ha).

A large source of variance is in precipitation samples representing collection periods that span sequential months (mostly winter months). On average, a precipitation sample retrieved at the beginning of a month (e.g., within the first week of the month) can contain some proportion of water that fell in the previous month (depending on when the prior sample was retrieved). To date, samples spanning sequential months generally have been assigned entirely to the month in which the sample was retrieved. Doing so, however, causes the precipitation amount (and associated air-pollutant deposition mass) to be biased high in the current month and biased low in the previous month, on average. Depending on when samples are retrieved, and the duration of the interval collection period, this error can propagate to substantial proportions. Coordinating GRSM precipitation monitoring data with independent precipitation data from sources such as the National Weather Bureau or the National Park Service at GRSM is a labor-intensive method of determining a realistic distribution pattern between sample collection dates. A more practical, and defensible, method of allocating the amount of precipitation in a given sample among adjoining months is to proportion measured precipitation volumes by day.

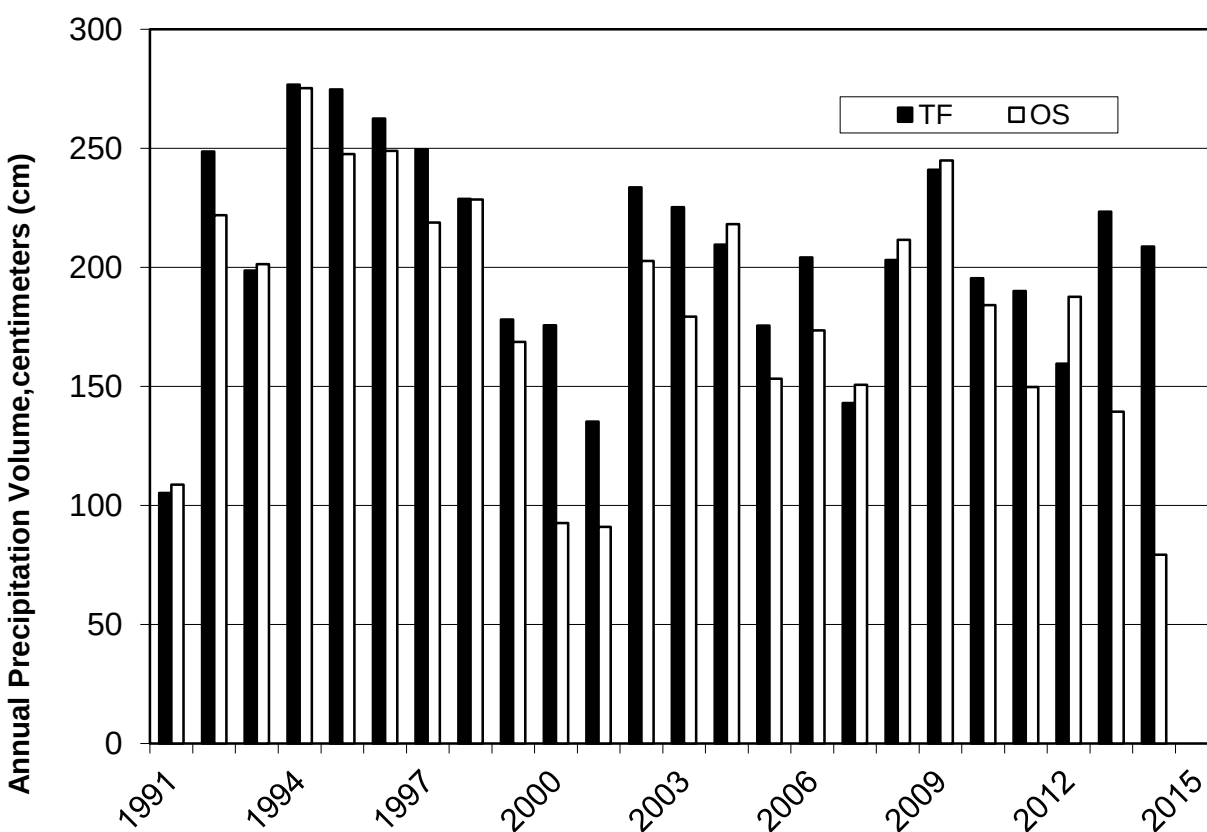


Figure 2. Total annual precipitation volumes (in centimeters) at throughfall (TF) and open site (OS) in the NDW. Sampling in 1991 began mid-year; that year's data do not represent the entire year.

Stream water quality and discharge are measured at the watershed outlet of NDW, in two adjacent “streamlets,” the southwest (SW) and northeast (NE) streams. At each streamlet, flows are obtained from continuous data collected with 3-ft H-flume and GlobalWater® WL16 stage recorders. Stage recorders measure flow depth every 15 minutes, and discharge is computed from measured water depth through the standard USDA H-flume formulas. Water quality parameters (pH, conductivity and temperature) are continuously monitored (at 15-minute intervals) with Eureka Manta II sondes: data collection in the SW started in July 1991, and in the NE in April 1998. Grab samples of stream water are collected from the NE and SW streams every two weeks for chemical analyses.

Soil water samples are collected from three soil horizons (A, B_w, and C_b) through 12 suction lysimeters (four per soil horizon), located adjacent to the TF site within the electric fenced area (Figure 1). Suction lysimeters (Model SW-074; SMS, Inc.) are constructed of porous stainless steel, with dimensions of 0.875 inch outside diameter and 4.5 inches in length (the length of the porous section is 3.7 inches). A small battery-powered vacuum pump creates the negative pressure to the lysimeters through thick-walled plastic bottles that pulls soil water from the site. Actual volumes of soil water collected through the lysimeters vary widely based on rainfall patterns.

All NDW water samples were transported to the UTK-CEE WQ laboratory to be analyzed for the chemistry parameters listed in Appendix B; corresponding analytical methods also are listed. Data quality was evaluated and documented through a program of QA checks for all analyses (Section 4.0). The NDW grab sample dataset for 2014 consists of 114 samples: 15 samples from OS, 22 samples from TF, 24 samples each from the NE and SW streamlets, and 29 from the three soil lysimeter horizons. The following sections summarize the 2014 data, and the comparison between them and historical NDW data collected between 1991 and 2013.

2.3 Annual Precipitation Volume

Precipitation volumes collected during 2014 were 209 cm at the TF and 79 cm at the OS (Figure 2). Annual cumulative precipitation volumes in all prior years (excluding the partial first year of data collection, 1991) ranged between 135 and 277 cm at TF and between 91 and 275 cm at OS. OS precipitation collected between April and December 2014 appears to have been a low-precipitation period for NDW direct precipitation; however, when fog/mist precipitation is included (i.e., the TF volume), 2014 appears to have been a typical year. Note that a few months of precipitation data were not collected at OS in 2000 and 2001; precipitation volumes are underestimated for those years.

2.3.1 Seasonal Precipitation Patterns

Seasonal precipitation patterns are relevant to acid-pollutant deposition in the Park; higher amounts of precipitation result in higher wet-deposition mass-loading of pollutants. Monthly precipitation totals were averaged over all years of record (since 1991) (Figure 3). The error-bars represent the 95% confidence interval of the mean. A clear seasonal pattern is evident, with nearly twice as much precipitation falling in winter months (January) than in summer months (July). The effect of canopy interception and evaporation in NDW is seen by the lower amounts of precipitation reaching the understory in summer months (OS volume minus TF volume).

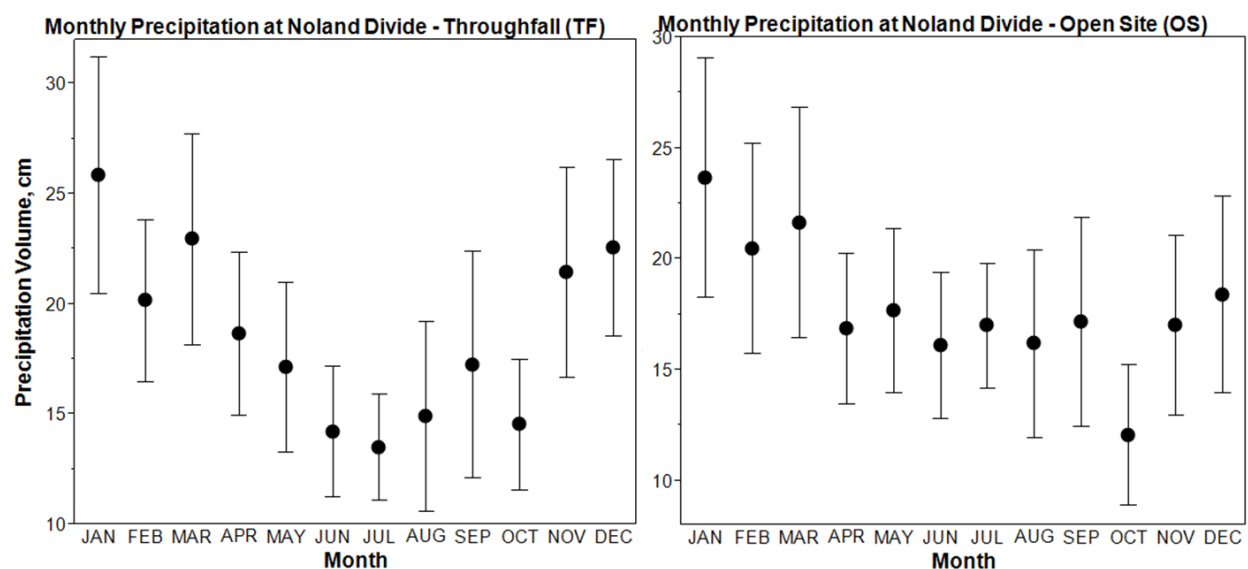


Figure 3. Distribution of monthly precipitation totals, averaged over all years (1991 to present). Error bars represent 95% confidence intervals of the mean precipitation volume (in centimeters).

2.3.2 Precipitation pH Profile

The seminal chemistry parameter for acidification is pH. Summarizing pH over spatial or temporal scales involves calculating mean values; however, the concept of “mean pH” is not trivial for a parameter (proton activity) that varies geometrically (i.e., in powers of 10; or on a log-scale). The mean of a geometric parameter is numerically equivalent to taking the arithmetic mean of the log-transformed value. Since pH is a log-transform of proton activity, it is appropriate to calculate mean pH as the arithmetic mean of pH values (Helsel 1984). This is the method used on GRSM pH data.

In 2014, the average pH of all TF samples was 5.10, and the pH of individual TF samples ranged between 4.29 (March) to 6.08 (September). Over the period of record (1991-2014), the 2014 pH data for TF represented the fourth highest annual average pH, the third highest monthly minimum pH, and the second highest monthly maximum pH, to date (Figure 4). The average pH of all OS samples was 5.40, and the pH of individual OS samples ranged from 4.96 (June) to 5.99 (July). Over the period of record, the 2014 pH data for OS represent the fifth highest annual average pH, the fourth highest monthly minimum pH, and the ninth highest monthly maximum pH, to date.

The pH of NDW precipitation has increased from the initial (1991) lows of 3.98 and 4.35 in TF and OS, respectively, to their current values (Figure 4). Between 2007 and 2008, the pH of TF and OS precipitation increased dramatically. Except for the anomalous year of 2013, the average pH of TF has been lower than OS by half-pH unit (on average), but the spread in average monthly pH values results in some overlap in year-to-year ranges.

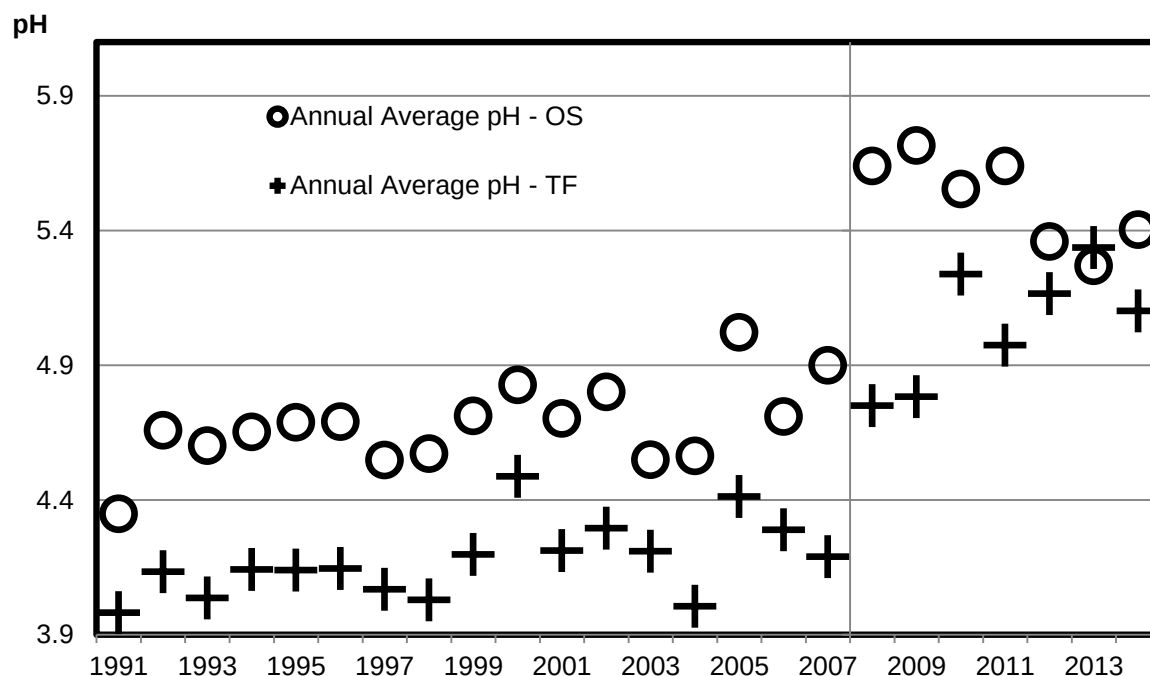


Figure 4. Annual mean pH of precipitation collected at TF (crosses) and OS (open circles).

2.4 Annual Deposition Rates for Chemical Constituents

Annual rates of deposition of sulfur and nitrogen species into the NDW were computed for both TF and OS. These deposition data are presented in two units: mass equivalents per hectare per year (eq/ha/yr) and kilograms per hectare per year (kg/ha/yr). Data for all years of study are summarized below to assess possible trends in the long-term deposition into NDW.

2.4.1 Sulfate Deposition Profile

During 2014, the deposition of sulfate was estimated to be 681 eq/ha/yr (32.7 kg-SO₄/ha/yr) at the TF site, and 258 eq/ha/yr (12.4 kg-SO₄/ha/yr) at the OS site (Figure 5). These deposition rates were the fifth lowest amount measured at TF and the fourth lowest amount measured at OS, during the period of record. Deposition is highly dependent on rainfall volumes; i.e., mass of pollutants collected through precipitation during drought years will be less than during wet years. However, despite annual precipitation amounts remaining fairly constant since 2007-2008, the six lowest measured sulfate deposition rates at TF have been recorded in that same period of time. Thus, this deposition trend is not random, and likely has been caused by decreased pollutant loadings to the atmosphere.

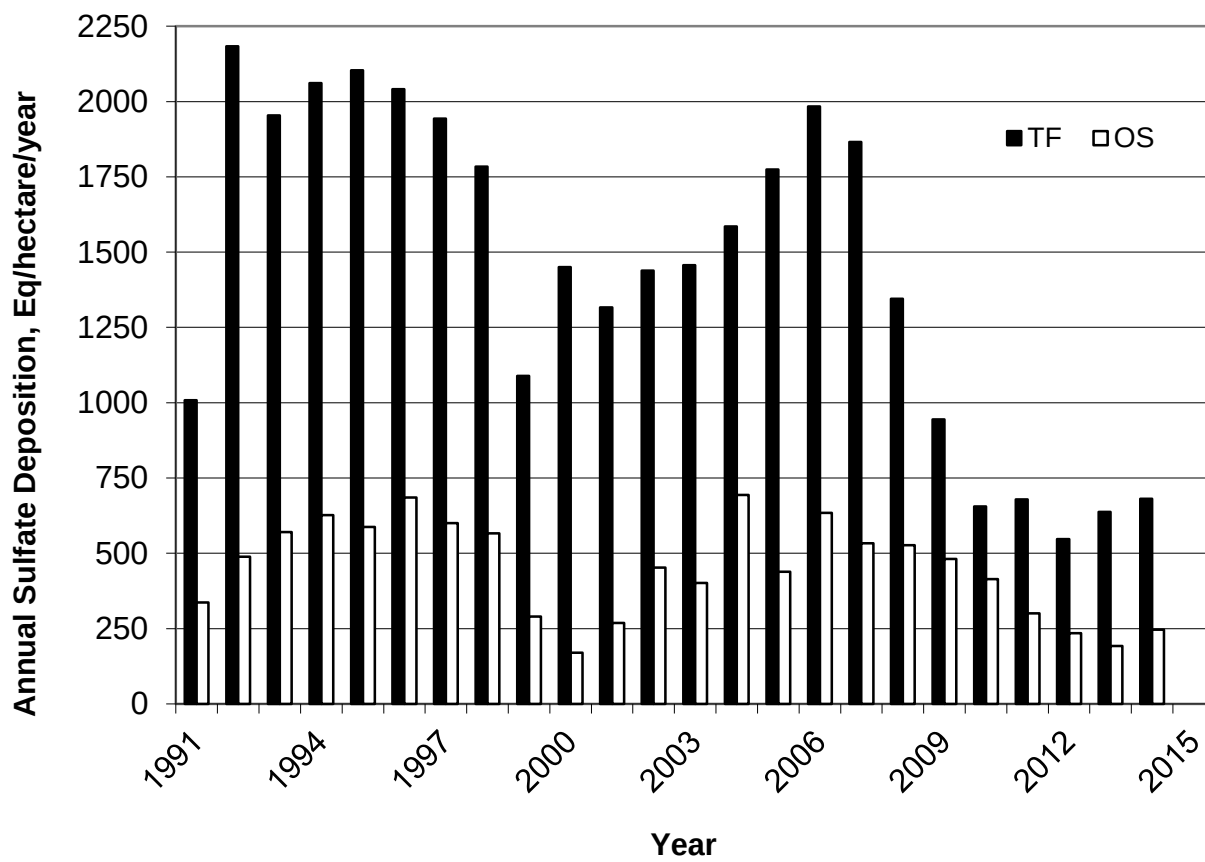


Figure 5. Total sulfate (in equivalents per hectare per year; eq/ha/yr) entering NDW via precipitation measured at TF and OS. Sampling in 1991 began mid-year; those data do not represent the entire year.

2.4.2 Nitrogen Deposition Profile

During 2014, the deposition rate (mass per unit area) of total inorganic nitrogen (T.I.N.; nitrate plus ammonium) into the NDW was 896 eq/ha/yr (40.7 kg/ha/yr) at the TF and 401 eq/ha/yr (17.2 kg/ha/yr) at the OS (Figure 6). These rates were substantial increases from 2013, but are in the ranges observed for years after 2007. Note that this year's calculated cumulative deposition rate of T.I.N. at the TF site was dominated by uncharacteristically high nitrate and ammonium concentrations in two samples from March and November of this year.

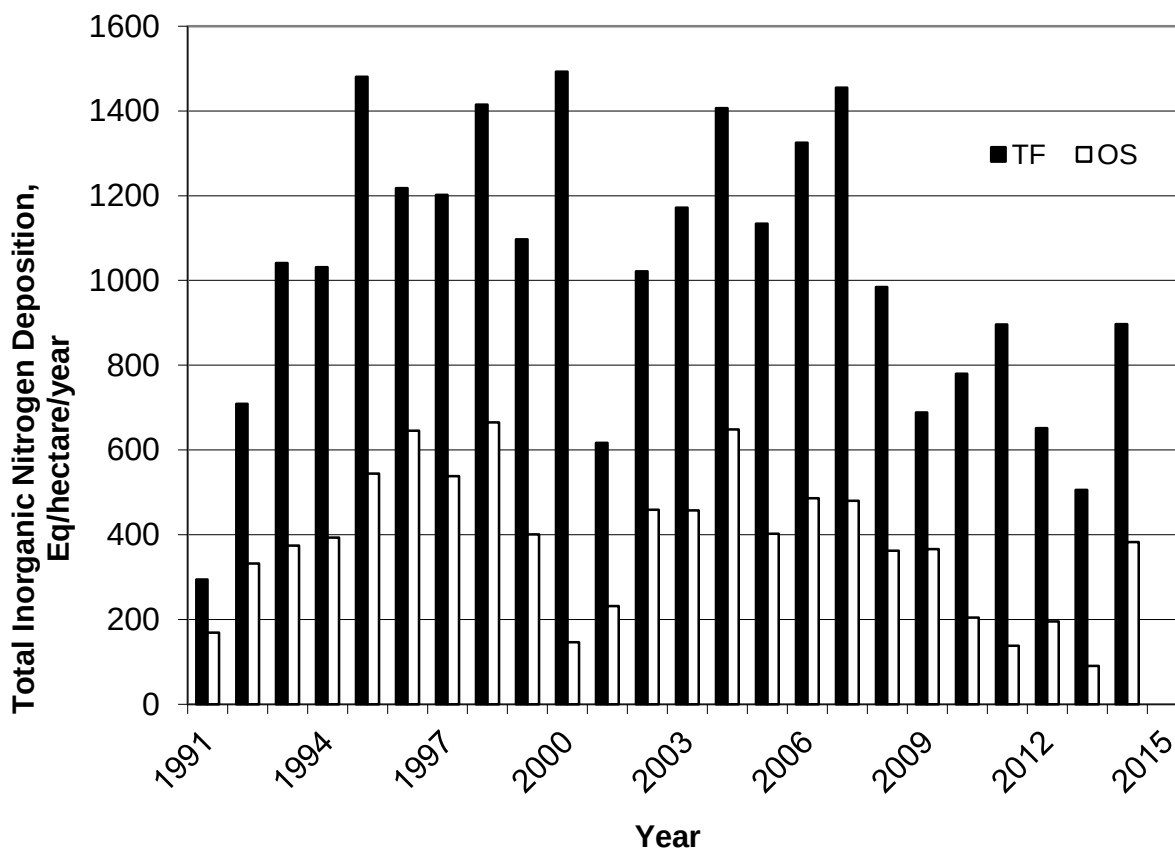


Figure 2. Total inorganic nitrogen (nitrate + ammonium; eq/ha/yr) entering NDW via precipitation measured at TF and OS. Sampling in 1991 began mid-year; those data do not represent the entire year.

2.4.3 Nitrogen Speciation Shift

Closer inspection of the T.I.N. deposition data revealed an interesting relationship in the nitrogen speciation over time. Using TF data, the percentage of ammonium in the cumulative annual T.I.N. deposition was plotted over the period of record overlaid with the average annual pH of TF precipitation (Figure 7). Ammonium fraction of T.I.N. and the pH of TF precipitation appeared to be temporally correlated per visual inspection where the ratio of ammonium-to-nitrate increases with TF precipitation pH. More investigation is needed to confirm this relationship and to propose plausible explanations. Also, it can be inferred from equilibrium chemistry principles that the ratio of ammonium (ionized) to ammonia (un-ionized) concentrations in TF samples will be influenced by the precipitation pH, with ammonium predominating at lower pH conditions.

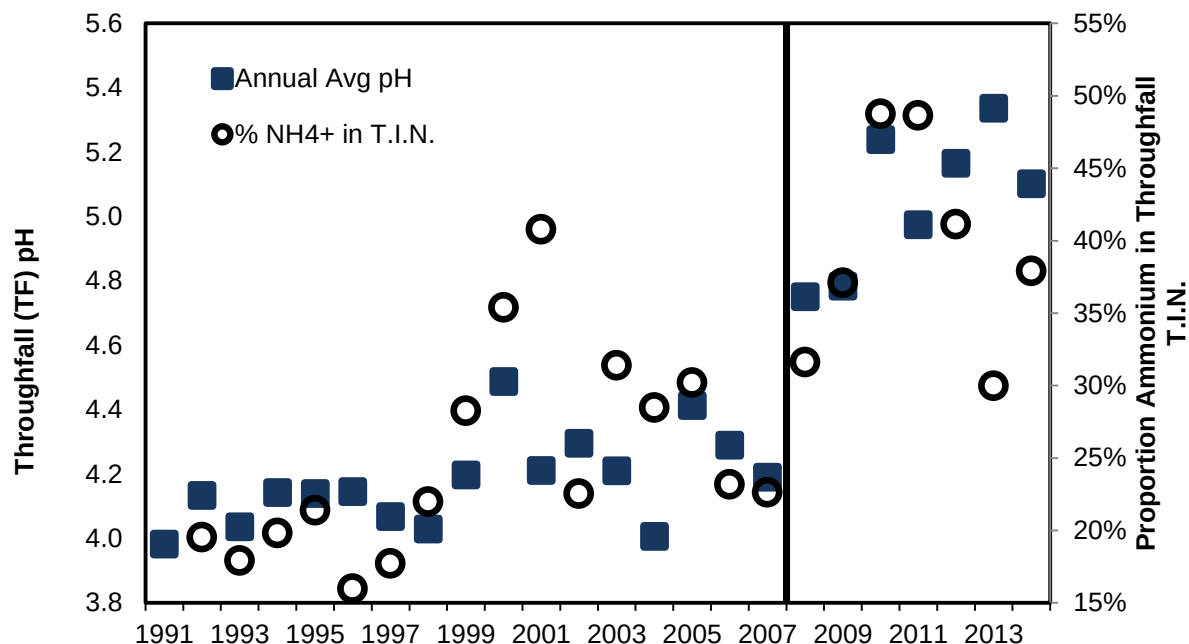


Figure 7. Annual mean percentage of ammonium in T.I.N. in TF precipitation, and the corresponding annual mean pH. Left axis is pH; right axis is percent ammonium in T.I.N. Sampling in 1991 began mid-year; that year's data do not represent the entire year.

2.5 Soil Water Chemistry

Soil water samples were collected periodically from lysimeters placed at three depths: A horizon at 8 cm (upper); B_w horizon at 35 cm (middle); and C_b horizon at 65 cm (lower). Soil water volumes collected in 2014 were 7.74 liters (L), 5.41 L, and 3.65 L from the upper, middle, and lower lysimeters, respectively. Soil water chemistry for all monitoring years are summarized in Table 1. In all three soil horizons, the mean 2014 soil water pH (4.57, 4.53 and 4.56, respectively) was greater than the overall mean pH for all prior years (4.04, 4.36 and 4.49, respectively). Soil pH is known to be highly correlated to carbonic acid (H₂CO₃*) concentration in soil water, and H₂CO₃* is formed from the dissolution of carbon dioxide (CO₂) in the soil gas phase. Concentrations of CO₂ usually are greater in soil than in the atmosphere because of local CO₂ production by microbial biodegradation of soil organic-matter (EPA 2002; Van Miegroet and Cole 1984). The general trend of increasing pH (decreasing acidity) with depth below surface reflects the lower organic carbon content and the correlated decrease in microbial activity in deeper soil. This general trend is evident in long-term mean pH of NDW soil horizons, but was not strong in 2014.

Mean ion concentrations in 2014 were less than corresponding mean values over all prior years. Anion concentrations did not appear to vary much with soil depth; calculated means were within the range of individual sample measurements. The same was observed for base cation concentrations in the soil water at the three soil horizons.

2.6 Stream Water Chemistry

NDW stream water samples (N = 24) were collected from the SW and NE streamlets in 2014; no collection trips were cancelled due to extreme winter conditions. The acidity profile of NE showed fairly consistent pH and ANC over the year based on the reported range indicating minimal seasonal patterns in water chemistry (Table 2). The pH of NE streamlet samples never exceeded 5.75 in the first half of 2014, and never dropped below 5.62 in the second half of the year. Except for one anomalously high ANC value (21.7 $\mu\text{eq/L}$ for the June 19 sample), the NE streamlet ANC ranged between 5.7 and 14.9 $\mu\text{eq/L}$. In the SW streamlet, stream pH and ANC were consistent throughout the year. Except for one anomalously high pH value (6.85 for the June 19 sample), SW streamlet pH ranged between 5.63 and 6.16, and showed no seasonal pattern. SW streamlet ANC values ranged between 11.8 and 21.5 $\mu\text{eq/L}$, except for two samples (June 19 and September 11) that had anomalously high ANC values (31.2 and 26.4 $\mu\text{eq/L}$, respectively).

Table 1. Summary data statistics for conductivity, pH, common anions and base cations in soil lysimeter samples collected in the current year, and in all prior years.

Chemistry *	Year(s) and Statistics	Upper = A horizon	Middle = Bw horizon	Lower = Cb horizon
Conductivity	2014 Mean (SE)	26.2 (1.0)	28.0 (3.5)	27.1 (0.4)
	1991-2013 Mean (SE)	63.9 (2.6)	39.3 (1.4)	33.4 (0.70)
pH	2014 Mean (SE)	4.57 (0.04)	4.53 (0.4)	4.56 (0.04)
	1991-2013 Mean (SE)	4.04 (0.02)	4.36 (0.02)	4.49 (0.01)
ANC	2014 Mean (SE)	-28.9 (7.3)	-32.5 (8.0)	-29.1 (11.3)
	2005-2013** Mean (SE)	-10.9 (2.6)	-18.4 (1.6)	-25.4 (1.9)
Chloride	2014 Mean (SE)	14.5 (1.1)	17.6 (2.0)	13.8 (1.5)
	1991-2013 Mean (SE)	28.4 (2.3)	27.9 (1.9)	23.4 (1.7)
Nitrate	2014 Mean (SE)	52.2 (5.1)	44.8 (7.8)	62.4 (2.7)
	1991-2013 Mean (SE)	136.7 (10.6)	73.2 (4.4)	82.3 (3.7)
Sulfate	2014 Mean (SE)	54.9 (5.7)	60.8 (7.0)	40.4 (1.4)
	1991-2013 Mean (SE)	91.2 (3.3)	95.1 (2.4)	89.6 (1.6)
Sodium	2014 Mean (SE)	15.0 (0.6)	16.2 (1.3)	17.1 (1.5)
	1991-2013 Mean (SE)	26.2 (3.4)	24.3 (0.92)	19.8 (0.68)
Potassium	2014 Mean (SE)	6.41 (0.6)	8.73 (0.9)	7.73 (0.6)
	1991-2013 Mean (SE)	22.3 (1.6)	11.1 (1.1)	9.87 (0.93)
Magnesium	2014 Mean (SE)	15.0 (1.0)	16.2 (0.9)	18.4 (0.3)
	1991-2013 Mean (SE)	26.5 (3.3)	20.2 (0.58)	23.9 (0.67)
Calcium	2014 Mean (SE)	14.4 (1.2)	17.7 (1.9)	22.9 (1.4)
	1991-2013 Mean (SE)	50.9 (7.6)	26.9 (1.1)	38.8 (2.3)

* Conductivity in micro-siemens per centimeter ($\mu\text{S/cm}$); concentrations in micro-equivalents per liter ($\mu\text{eq/L}$)

** Acid-neutralizing capacity (ANC) was added to the analytical suite for this project in 2005.

SE = standard error of the mean value.

NE stream water had lower pH and ANC, and higher ion concentrations, than SW. Differences in means were tested for significance, and it was found that the streams' mean ANC were statistically significantly different at the 95% confidence level ($p = 0.002$). This difference between NE and SW ANC has been observed consistently in prior monitoring years. The same significance test for pH *did not* suggest statistically significant differences in pH at $\alpha = 0.05$, although the pH in SW consistently averaged 0.2 pH units greater than pH in NE. With the exception of nitrate and calcium, the 2014 annual means were slightly smaller than overall mean values for pre-2014 data.

Table 2. Summary data statistics for conductivity, pH, common anions and base cations in streamlet water samples (NE and SW) collected in the current year, and in all prior years.

Chemistry *	Year(s) and Statistics	NE Streamlet	SW Streamlet
Conductivity	2014 Mean (SE)	12.8 (0.1)	11.6 (0.08)
	1991-2013 Mean (SE)	14.8 (0.08)	12.9 (0.13)
pH	2014 Mean (SE)	5.72 (0.03)	5.94 (0.05)
	1991-2013 Mean (SE)	5.61 (0.01)	5.86 (0.01)
ANC	2014 Mean (SE)	9.97 (0.7)	17.7 (0.8)
	2005-2013** Mean (SE)	4.34 (0.24)	11.7 (0.27)
Chloride	2014 Mean (SE)	13.5 (0.4)	11.7 (1.0)
	1991-2013 Mean (SE)	18.0 (0.38)	15.3 (0.37)
Nitrate	2014 Mean (SE)	21.3 (0.4)	20.1 (0.9)
	1991-2013 Mean (SE)	44.4 (0.35)	39.1 (0.32)
Sulfate	2014 Mean (SE)	44.6 (1.6)	37.5 (2.2)
	1991-2013 Mean (SE)	41.3 (0.26)	30.2 (0.21)
Sodium	2014 Mean (SE)	23.2 (0.5)	22.4 (0.3)
	1991-2013 Mean (SE)	25.4 (0.24)	25.4 (0.20)
Potassium	2014 Mean (SE)	9.44 (0.3)	6.98 (0.3)
	1991-2013 Mean (SE)	11.4 (0.26)	8.67 (0.20)
Magnesium	2014 Mean (SE)	17.2 (0.4)	16.7 (0.3)
	1991-2013 Mean (SE)	20.1 (0.16)	17.8 (0.15)
Calcium	2014 Mean (SE)	42.0 (0.5)	40.5 (0.5)
	1991-2013 Mean (SE)	50.9 (0.37)	46.2 (0.29)

* Conductivity in micro-siemens per centimeter ($\mu\text{S}/\text{cm}$); concentrations in micro-equivalents per liter ($\mu\text{eq}/\text{L}$)

** Acid-neutralizing capacity (ANC) was added to the analytical suite for this project in 2005.

SE = standard error of the mean

3.0 Park-wide Stream Survey

Park-wide stream survey (also termed long-term synoptic stream WQ monitoring) began in October 1993 to monitor water quality in GRSM streams, and simultaneously assess possible correlations between GRSM water chemistry and atmospheric sources of acid-generating pollutants. Currently active sampling sites are distributed among seven watershed drainage basins identified by their predominant surface water body (Figure 8): Abrams Creek (4 sites); Cataloochee Creek (8 sites); Cosby Creek (4); Little River (3); Oconaluftee River (5); Road Prong/Rt.6 (8); and Hazel Creek (11). In 2013, 197 samples were collected from these locations and analyzed for chemical parameters. These seven drainage basins were selected to best represent the natural spatial variability in elevation, geology types, and land use/disturbance histories found in the GRSM (Odom 2003). Location information for these sites is listed in Appendix C.

3.1 Park-Wide Water Chemistry: Watershed Summary

The water chemistry dataset of the GRSM monitoring program was evaluated for trends and correlations. The combined Park-wide water chemistry dataset has been assessed for patterns and trends (e.g., Robinson et al. 2008), but the high degree of variability observed in the combined dataset limited what conclusions could be drawn from that assessment. With growing awareness of the influence of basin-specific factors on WQ (Neff et al. 2013), the dataset was reorganized and data analysis was done on a watershed basis. This approach has revealed interesting patterns and trends in stream water chemistries that were masked by a Park-wide data analysis approach. Summary statistics were calculated for the eight monitored watersheds and for 43 sampling sites included in the current monitoring program. Mean and standard error over the period of record were calculated for:

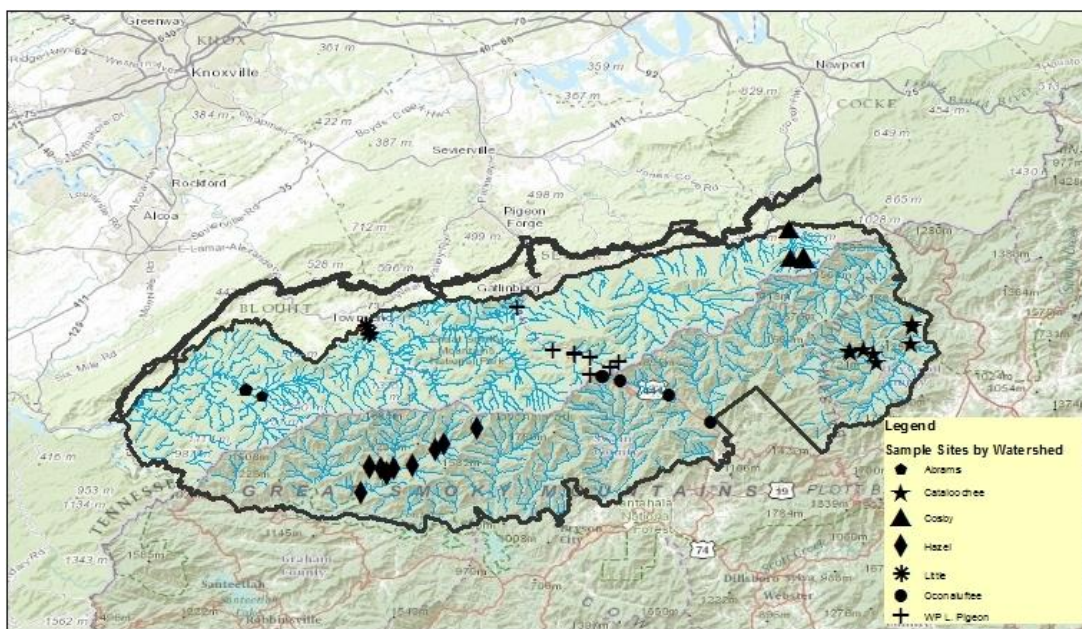


Figure 3. Currently sampled sites for the GRSM Park-wide stream survey water quality monitoring program. “WP L. Pigeon” includes Walker Prong, West Prong, and Road Prong as well as the West Prong of the Little Pigeon.

conductivity (“Cond.”; $\mu\text{S}/\text{cm}$), pH (standard unit), acid-neutralizing capacity ANC ($\mu\text{eq}/\text{L}$), sum of major anions ($\mu\text{eq}/\text{L}$; chloride, nitrate, sulfate), sum of base cations ($\mu\text{eq}/\text{L}$), and total inorganic solutes (TIS; $\mu\text{eq}/\text{L}$). The results are shown in Table 3.

Initially, data from all sampling sites within the Abrams Creek drainage basin were summarized together. On closer inspection, clear differences in water chemistry of individual sites warranted subdividing the Abrams Creek sites into Mill Creek (ABR Mill; Sites 173 and 488) and Abrams Creek (ABR Main; Sites 174 and 489). In the 2014 sampling period, overall ion charge balance

Table 2. Selected water chemistry for current year and all prior years, organized by watershed (standard error of the mean in parentheses). Note: Abrams Creek drainage basin is divided into three subsets, Mill Creek sampling sites, Main Stem sampling sites, and sites designated by “ABC”.

Drainage Basin (Data Years)	Cond. $\mu\text{S}/\text{cm}$	pH	ANC $\mu\text{eq}/\text{L}$	$\Sigma(\text{anions})$ $\mu\text{eq}/\text{L}$	$\Sigma(\text{cations})$ $\mu\text{eq}/\text{L}$	TIS $\mu\text{eq}/\text{L}$	Charge Balance
West Prong Little Pigeon River (2014)	22.2 (1.17)	5.84 (0.02)	66.1 (7.67)	123.5 (5.76)	186.7 (10.6)	379.3 (22.1)	2.10%
(1993 – 2013)	19.7 (0.24)	6.02 (0.03)	31.0 (1.78)	120.4 (1.44)	104.8 (5.74)	257.9 (6.74)	
Cosby Creek (2014)	16.1 (0.54)	5.77 (0.05)	23.3 (2.80)	100.0 (2.83)	132.4 (3.89)	259.8 (7.94)	2.64%
(1993 – 2013)	16.0 (0.24)	6.11 (0.02)	27.5 (1.49)	95.8 (1.61)	100.3 (4.24)	225.3 (4.77)	
Oconaluftee (2014)	23.4 (2.96)	5.76 (0.10)	45.1 (8.30)	148.1 (26.5)	196.1 (20.0)	394.7 (41.4)	0.82%
(1993 – 2013)	27.0 (0.87)	6.16 (0.03)	45.9 (2.33)	175.9 (5.89)	153.9 (7.27)	377.0 (8.83)	
Hazel Creek (2014)	11.8 (0.36)	6.18 (0.04)	65.2 (4.88)	40.8 (1.40)	115.0 (4.69)	222.4 (9.14)	0.35%
(1993 – 2013)	12.8 (0.25)	6.49 (0.03)	73.6 (2.07)	43.5 (1.06)	91.9 (4.84)	208.6 (5.88)	
Cataloochee (2014)	14.7 (0.42)	6.15 (0.03)	73.3 (4.76)	52.1 (2.47)	131.1 (5.02)	258.0 (9.57)	0.43%
(1993 – 2013)	13.8 (0.17)	6.61 (0.02)	76.1 (1.62)	45.8 (0.74)	101.2 (3.43)	222.4 (4.18)	
Little River (2014)	17.2 (0.73)	6.01 (0.06)	77.6 (9.22)	59.4 (3.08)	150.8 (8.28)	293.4 (16.8)	1.87%
(1993 – 2013)	18.9 (0.44)	6.73 (0.03)	114.7 (4.53)	60.9 (1.03)	138.8 (6.94)	314.9 (9.41)	
ABR Mill (2014)	13.8 (0.59)	6.34 (0.14)	66.4 (6.24)	46.5 (2.13)	123.7 (6.87)	238.0 (12.6)	4.47%
(1993 – 2013)	18.4 (1.10)	6.62 (0.03)	115.9 (12.0)	54.7 (1.36)	140.4 (12.2)	307.9 (23.1)	
ABR (ABC) (2014)	20.1 (6.84)	6.19 (0.17)	32.8 (4.90)	61.1 (3.11)	204.4 (90.4)	300.4 (89.0)	Strong HCO_3^- influence
No Previous Data							
ABR Main (2014)	110.7 (5.40)	7.34 (0.09)	96.8 (22.7) **	78.6 (2.08)	1177.1 (58.0)	1378.3 (78.1)	Strong HCO_3^- influence
(1993 – 2013)	95.3 (3.46)	7.48 (0.04)	940.2 (35.8)	82.2 (1.43)	688.5 (50.9)	1701.4 (69.0)	

Notes: Cond. = conductivity; ABR = Abrams Creek; ANC = acid-neutralizing capacity; TIS = total inorganic solutes

* Distribution of individual measurements shows bimodal distribution. Subsets of sites within the watershed have substantially different mean conductivity, pH and/or ANC.

** Instrument software limitations apparently caused titrations of high-ANC samples to be truncated, resulting in gross underestimation of ANC concentrations in samples from Site 174 and 489. Visual evaluation of titration plots indicates an approximately 10-fold underestimation.

within each drainage basin was excellent (within 5.2%) for all eight drainage basins. All except Abrams Creek were slightly imbalanced to the negative, indicating the existence of one or more anions not accounted for by the analyses applied to these samples (e.g., phosphate, carbonate, organic acids, etc.). For most parameters, the levels observed in Abrams Creek sites far exceed those in the Mill Creek tributary sites, and in all other drainage basins. The positive ion imbalance (i.e., excess anions) and high dissolved solids content in Abrams Creek can be explained by the dissolution of limestone-karst minerals from the surrounding soil and from the bedrock underlying this part of the Park. Collectively at the watershed scale, the 2014 mean pH in all eight drainage basins was greater than, or equal to, the overall mean pH for all prior years. Corresponding to pH shifts, mean ANC in five drainage basins was greater than the mean ANC over all prior years. The mean concentrations of total dissolved ions in 2014, as reflected in total anions, total cations and total inorganic solutes, were greater than the overall mean concentration over all prior years in seven of the eight drainage basins (all except Mill Creek).

3.3.1 Abrams Creek Water Chemistry

Abrams Creek WQ data associated with four sampling locations (Sites 173, 174, 488 and 489) were available back to the beginning of the monitoring program (1993). As described earlier (Table 3), water chemistry of the four active Abrams Creek sampling sites were markedly different from all other monitored drainage basins, and closer evaluation of the data revealed clear differences among individual sites within the drainage basin. Table 4 summarizes the mean values (for current year and for all prior years) of water chemistry parameters for the four sampling sites, as well as each site's elevation in meters above mean sea level (m amsl).

Water chemistry from the upper reach of Abrams Creek was distinct from all other monitored locations in the GRSM. Sites 174 and 489 had the highest values for all chemistry parameters except “sum of chloride, nitrate and sulfate.” The apparent exception (ANC) is not real; method program limitations in the auto-titrator software unknowingly caused titrations of the high ANC samples to end prior to reaching endpoint. The truncated titrations yielded under-estimated ANC concentrations for high ANC samples, by a factor of ~10 as noted after visual examination of raw titration curve data. The instrument has been reprogrammed to handle samples with both low ANC (acidified water with negative or zero ANC) and high ANC (limestone-stream water samples).

Sites 174 and 489 were unique in having total base cation (sum of sodium, potassium, magnesium and calcium) and total inorganic solute (TIS) concentrations in the thousands ($\mu\text{eq/L}$), ANC at ~1000 $\mu\text{eq/L}$, and $\text{pH} > 7.4$. With such high TIS and base cation concentrations, it is curious to note that concentrations of measured anions (chloride, nitrate and sulfate) have not increased proportionally, and in fact remain at historic levels (back to 1993). The anions compensating for the large concentrations of cations in water at these sites must consist of unquantified species, likely dominated by bicarbonate (which is clearly observed in raw ion chromatographs from anion analyses; *data not shown*). It is also notable that the mean pH in 2013 was substantially greater than the overall mean over all prior years, suggesting that pH continues to increase even in GRSM streams that have large amounts of native ANC. The Mill Creek tributary system feeds into the Abrams Creek, upstream of Site 489. The 2014 water chemistry at the two Mill Creek sites was similar to the

overall mean chemistry over all prior years. There appears to be some difference in water chemistry between the two Mill Creek sites.

With the exception of pH, all chemistry parameters in Site 173 were actually lower in 2014 as compared to the overall mean values over all prior years; stream pH was approximately equal within the measurement error. This trend was specific to Site 173 and might be evidence of biogeochemistry processes particular to the drainage area up-gradient of that location. Site 489 appeared to reflect the flow-weighted dilution effect that Mill Creek has on Abrams Creek water chemistry.

Table 4. Summary of water chemistry data for Abrams Creek sampling sites. Current year and mean of all prior years (standard error of the mean is shown in parentheses).

Sampling Site (Data Years)	Cond. µS/cm	pH	ANC µeq/L	Σ(anions) µeq/L	Σ(cations) µeq/L	TIS µeq/L	Elevation (m amsl)
Mill Creek sites							
Site 173 (2014) (1993 – 2013)	15.2 (0.67) 23.8 (2.02)	6.15 (0.08) 6.78 (0.03)	82.8 (4.85) 177.6 (22.5)	46.3 (3.13) 55.4 (1.67)	141.8 (5.89) 195.6 (24.0)	272.4 (10.1) 420.4 (45.9)	523
Site 488 (2014) (1993 – 2013)	12.4 (0.25) 12.0 (0.16)	6.54 (0.25) 6.43 (0.02)	50.1 (4.22) 46.0 (1.21)	46.8 (3.25) 54.2 (1.44)	105.5 (3.61) 98.3 (3.03)	203.5 (4.01) 198.7 (4.08)	546
Abrams Creek sites (Main Channel)							
Site 174 (2014) (1993 – 2013)	117.1 (6.48) 100.4 (4.19)	7.24 (0.15) 7.46 (0.05)	88.2 (27.7) ** 990.8 (44.6)	81.6 (2.83) 84.2 (1.63)	1260.7 (78.7) 750.0 (60.0)	1478.9 (94.9) 1817.9 (88.7)	523
	104.4 (8.29) 87.5 (3.24)	7.44 (0.08) 7.50 (0.04)	105.4 (39.8) ** 857.6 (35.6)	75.6 (2.66) 80.4 (1.54)	1093.5 (73.6) 765.9 (46.2)	1277.6 (112.9) 1692.3 (69.0)	521
Site 156 (2014)	61.1 N = 1	6.47 N = 1	28.4 N = 1	57.4 N = 1	655.9 N = 1	742.3 N = 1	684
Anthony Creek sites							
Site 423 (2014)	14.0 (0.20) n.a.	6.40 (0.32) n.a.	45.9 (3.11) n.a.	60.7 (6.57) n.a.	121.9 (6.49) n.a.	229.6 (8.62) n.a.	1,310
Site 200 (2014)	12.6 (0.05) n.a.	5.88 (0.07) n.a.	21.2 (1.65) n.a.	62.8 (4.55) n.a.	102.4 (9.56) n.a.	185.6 (11.1) n.a.	2,066

Notes: Cond. = conductivity; ANC = acid-neutralizing capacity; TIS = total inorganic solutes; m amsl = meters above mean sea level.

** Instrument software limitations apparently caused titrations of high-ANC samples to be truncated, resulting in gross underestimation of ANC concentrations in samples from Site 174 and 489. Visual evaluation of titration plots indicates an approximately 10-fold underestimation.

3.3.2 Cataloochee Creek Water Chemistry

Cataloochee Creek WQ data for eight sampling locations (Sites 142, 143, 144, 147, 148, 149, 293 and 493) were available since 1993. Table 5 summarizes the mean values (for current year and for all prior years) of water chemistry parameters for the eight sampling sites, and lists each site's elevation (m amsl). The sites are presented in sequence from upstream to downstream. Water chemistry was relatively consistent within the drainage basin; magnitudes did not vary drastically among the eight sampling sites. Stream pH did not show any obvious spatial patterns, and the range of mean values for 2014 spanned only ~0.4 pH units. In all eight sites, the mean pH for 2014 was greater than the overall mean for all prior years, by as much as 0.2 pH units at some sites, indicating continued increase of stream pH in this drainage basin. In six of the eight sites, the mean ANC for 2014 was greater than the overall mean for all prior years, and in the two remaining sites, ANC for 2014 was essentially equally to prior years' overall mean ANC, within measurement variability. In all cases, the mean base cation concentrations for 2014 were greater than prior years' overall mean. at Site 4. It was unclear why the water chemistry is different between the two Rock Creek sampling locations.

Table 5. Summary of water chemistry data for Cataloochee Creek sampling sites. Current year mean and mean of all prior years (standard error of the mean is shown in parentheses).

Sampling Site (Data Years)	Cond. $\mu\text{S/cm}$	pH	ANC $\mu\text{eq/L}$	$\Sigma(\text{anions})$ $\mu\text{eq/L}$	$\Sigma(\text{cations})$ $\mu\text{eq/L}$	TIS $\mu\text{eq/L}$	Elevation (m amsl)
Site 142 (2014) (1993 – 2013)	11.2 (0.36)	6.06 (0.12)	47.8 (7.74)	40.6 (2.80)	92.9 (5.20)	183.2 (11.7)	1006
	11.1 (0.18)	6.55 (0.02)	57.5 (1.60)	38.3 (0.85)	89.5 (3.00)	185.4 (3.69)	
Site 143 (2014) (1993 – 2013)	10.5 (0.29)	6.00 (0.11)	39.7 (6.76)	45.4 (2.74)	85.5 (5.15)	172.9 (11.6)	1,000
	10.8 (0.17)	6.44 (0.03)	48.1 (1.59)	42.8 (0.75)	83.6 (2.66)	175.0 (3.25)	
Site 144 (2014) (1993 – 2013)	11.8 (0.49)	6.12 (0.11)	49.2 (6.43)	44.3 (2.94)	99.3 (6.52)	194.5 (8.33)	911
	11.3 (0.22)	6.50 (0.02)	53.2 (1.55)	43.2 (1.34)	89.3 (2.94)	191.0 (7.24)	
Site 493 (2014) (1993 – 2013)	12.8 (0.58)	6.08 (0.10)	60.3 (7.86)	43.7 (1.91)	108.2 (6.61)	214.0 (14.3)	866
	12.5 (0.29)	6.57 (0.03)	66.6 (2.28)	42.0 (1.01)	104.3 (2.92)	212.7 (4.23)	
Site 149 (2014) (1993 – 2013)	15.5 (0.57)	6.10 (0.09)	82.5 (8.89)	64.3 (14.6)	140.8 (8.07)	289.4 (15.1)	777
	14.6 (0.18)	6.66 (0.02)	80.7 (1.96)	46.5 (0.88)	119.7 (3.77)	246.4 (4.71)	
Site 147 (2014) (1993 – 2013)	15.6 (0.54)	6.16 (0.07)	77.0 (6.67)	49.8 (2.81)	143.5 (8.92)	271.9 (12.7)	750
	14.7 (0.22)	6.66 (0.02)	82.9 (2.04)	47.2 (0.94)	117.6 (4.04)	264.9 (12.4)	
Site 148 (2014) (1993 – 2013)	18.2 (0.92)	6.26 (0.08)	133.1 (10.1)	50.1 (8.02)	175.0 (12.6)	359.4 (10.1)	754
	17.1 (0.26)	6.81 (0.03)	122.1 (3.04)	42.0 (1.67)	152.9 (4.62)	313.7 (6.78)	
Site 293 (2014)	17.3 (0.41)	6.19 (0.08)	76.1 (6.01)	62.4 (2.74)	158.2 (9.06)	298.2 (12.3)	840
	16.6 (0.17)	6.65 (0.02)	84.7 (1.85)	62.8 (1.41)	128.2 (4.57)	273.8 (5.84)	

Notes: Cond. = conductivity; ANC = acid-neutralizing capacity; TIS = total inorganic solutes; m amsl = meters above mean sea level.

3.3.3 Cosby Creek Water Chemistry

Cosby Creek WQ data for four sampling locations (sites 4, 114, 137 and 492) were available back to program inception (1993). Table 6 summarizes the mean values for water quality parameters at the four sampling sites for the current year (2014) and for all prior years, and lists the site elevations (m amsl). The sites are located in pairs on adjacent branches of this drainage basin: Sites 4 and 137 are located in Rock Creek; Sites 492 and 114 are located on the main stem of Cosby Creek. The spatial relationships among these sites explain much of the water chemistry of associated samples. Sites 4 and 137 have similar water chemistry, and Sites 114 and 492 have similar chemistry, with respect to conductivity, pH, ANC, base cation concentrations, and TIS.

The mean pH of Rock Creek stream water was about 6.0 in 2014, which is consistent with these sites' overall mean pH for all prior years. The pH at Site 4 in 2014 is slightly less than prior years' mean pH, but these were essentially equal within the measurement variability. The mean stream pH at sites in the main stem of Cosby Creek was 6.40 and 6.42, respectively. The mean pH at Sites 492, 114 and 137 in 2014 was greater than their overall mean pH in prior years. This indicates improving stream pH in the main stem of Cosby Creek and in the upper reaches of Rock Creek.

The corresponding water chemistry parameter, ANC, showed patterns consistent with the stream pH data at these sites. The mean ANC in stream water from the Rock Creek sites were similar in magnitude (12.7 and 13.7 $\mu\text{eq/L}$), and the mean ANC at the main stem sites were similar in magnitude (35.0 and 33.8 $\mu\text{eq/L}$). The ANC at the upper Rock Creek site (137) and in the two main stem sites in 2013 was marginally greater than prior years' mean ANC, although the differences were within measurement variability. In contrast, the mean ANC at Site 4 in 2014 was less than the mean of all prior years. Similarly, the mean TIS concentrations in 2014 were greater than prior years' overall mean TIS at Sites 137, 492 and 114, but were less than prior years' overall mean at Site 4. Conversely, the mean sum-of-anions (chloride, nitrate and sulfate) in 2014 were less than prior years' mean anions concentration at Sites 137, 492 and 114, but was greater than prior years' overall mean at Site 4. It was unclear why the water chemistry is different between the two Rock Creek sampling locations.

Table 6. Summary of water chemistry data for Cosby Creek sampling sites. Current year and mean of all prior years (standard error of the mean is shown in parentheses).

Sampling Site (Data Years)	Cond. $\mu\text{S/cm}$	pH	ANC $\mu\text{eq/L}$	$\Sigma(\text{anions})$ $\mu\text{eq/L}$	$\Sigma(\text{cations})$ $\mu\text{eq/L}$	TIS $\mu\text{eq/L}$	Elevation (m amsl)
Site 137 (2014)	15.6 (0.39)	5.64 (0.09)	11.1 (0.98)	98.2 (4.84)	119.4 (3.26)	233.8 (8.40)	838
(1993 – 2013)	15.1 (0.18)	5.84 (0.02)	10.5 (0.84)	101.4 (1.49)	95.7 (3.91)	208.9 (4.71)	
Site 4 (2014)	14.5 (0.55)	5.68 (0.07)	20.1 (8.74)	86.2 (4.37)	114.3 (7.06)	225.1 (15.4)	634
(1993 – 2013)	13.9 (0.25)	6.04 (0.04)	32.8 (3.73)	76.4 (3.00)	98.9 (3.79)	210.3 (4.86)	
Site 492 (2014)	16.1 (1.91)	5.85 (0.11)	31.4 (2.66)	106.3 (5.19)	147.0 (4.21)	288.1 (9.22)	832
(1993 – 2013)	17.4 (0.29)	6.26 (0.03)	31.0 (1.22)	105.1 (1.57)	124.0 (4.75)	261.0 (5.72)	
Site 114 (2014)	18.0 (0.24)	5.89 (0.09)	30.7 (2.07)	109.4 (3.64)	149.2 (1.67)	292.2 (4.47)	765
(1993 – 2013)	17.2 (0.33)	6.30 (0.02)	33.4 (1.51)	104.2 (1.43)	121.2 (4.88)	258.0 (5.56)	

Notes: Cond. = conductivity; ANC = acid-neutralizing capacity; TIS = total inorganic solutes; m amsl = meters above mean sea level.

3.3.4 Little River Water Chemistry

Little River WQ data for three sampling locations (Sites 13, 23 and 24) were available since the program began in 1993. Table 7 summarizes mean values of water quality parameters in the current year (2014) and in all prior years. Identifying correlations or drawing conclusions about overall water chemistry was difficult when comparing data from only three sites. Water chemistry at Sites 13 and 23 was similar to each other but both were marginally different from Site 24. Water pH in 2013 was greater than mean pH over all prior years. Uncharacteristically, the mean ANC at all three sites in 2013 was not greater (as expected with increasing pH) but marginally *lower* than prior years' mean ANC, although the differences were well within the measurement variability. The same pattern was evident for conductivity and sum of anions (chloride, nitrate and sulfate). Other sites

Table 3. Summary of water chemistry data for Little River sampling sites. Current year and mean of all prior years (standard error of the mean is shown in parentheses).

Sampling Site (Data Years)	Cond. μS/cm	pH	ANC μeq/L	Σ(anions) μeq/L	Σ(cations) μeq/L	TIS μeq/L	Elevation (m amsl)
Site 13 (2014)	17.5 (0.95)	6.09 (0.12)	99.3 (11.0)	55.1 (3.21)	160.5 (11.7)	316.9 (21.1)	335.3
(1993 – 2013)	17.9 (0.36)	6.71 (0.03)	102.8 (3.81)	60.1 (1.17)	131.9 (6.15)	295.2 (7.61)	
Site 23 (2014)	16.7 (1.31)	6.06 (0.14)	91.6 (13.4)	52.5 (2.77)	152.7 (15.6)	299.1 (27.9)	350.5
(1993 – 2013)	17.4 (0.54)	6.68 (0.03)	103.4 (5.70)	57.6 (1.51)	130.9 (7.53)	292.5 (11.4)	
Site 24 (2014)	23.4 (1.32)	6.19 (0.12)	146.6 (14.1)	62.3 (1.97)	219.9 (15.1)	430.3 (28.4)	350.5
(1993 – 2013)	22.0 (0.51)	6.82 (0.03)	139.4 (4.87)	65.1 (1.06)	161.2 (7.89)	366.0 (10.4)	

have been sampled a few times in 1994-1996 for a one-time WQ assessment.

3.3.5 Oconaluftee River Water Chemistry

The Oconaluftee River WQ dataset associated with five sampling locations (Sites 251, 252, 253, 268 and 270) included data back to 1993. Table 8 summarizes the mean values (for current year and for all prior years) of water chemistry parameters for the five sampling sites, and the site elevations. Sites are presented in upstream to downstream sequence. Stream chemistry in this drainage basin showed strong spatial trends, with higher concentrations of total dissolved solutes and lower pH and ANC at the upstream sites (253, 252, 251) than at the downstream sites (270 and 268). It is suspected that water chemistry at Site 253, which is immediately up-gradient of Site 252, is influenced by runoff from an adjacent parking area. However, the general trend in water chemistry is decreasing concentrations and increasing pH with distance downstream, suggesting a dilution and buffering effect by tributaries feeding the main stem.

The predominance of solutes leached from soil and bedrock in this drainage basin originates from sources near the headwaters. Samples collected from Site 252 in 2014 had the highest aluminum

(0.120 micromoles per liter; μM), copper (0.0012 μM), manganese (0.113 μM), and zinc (0.043 μM) concentrations.

Table 8. Summary of water chemistry data for Oconaluftee River sampling sites. Current year and mean of all prior years (standard error of the mean is shown in parentheses).

Sampling Site (Data Years)	Cond. $\mu\text{S}/\text{cm}$	pH	ANC $\mu\text{eq}/\text{L}$	$\Sigma(\text{anions})$ $\mu\text{eq}/\text{L}$	$\Sigma(\text{cations})$ $\mu\text{eq}/\text{L}$	TIS $\mu\text{eq}/\text{L}$	Elevation (m amsl)
Site 253 (2014)	24.2 (0.56)	6.05 (0.11)	84.1 (7.77)	122.7 (1.16)	215.4 (7.14)	424.1 (16.0)	1450.8
(1993 – 2013)	25.6 (0.95)	6.56 (0.04)	86.5 (2.18)	129.8 (5.95)	176.2 (8.54)	392.5 (12.4)	
Site 252 (2014)	40.4 (3.05)	5.11 (0.06)	-3.21 (3.12)	313.3 (23.7)	296.2 (22.9)	622.3 (42.4)	1426.4
(1993 – 2013)	45.2 (1.36)	5.33 (0.07)	16.0 (8.09)	325.1 (12.1)	241.9 (12.9)	618.6 (20.6)	
Site 251 (2014)	28.4 (0.33)	5.88 (0.12)	29.5 (1.22)	197.0 (1.70)	243.8 (4.90)	473.2 (6.92)	1222.2
(1993 – 2013)	29.8 (0.67)	6.15 (0.02)	24.5 (1.05)	212.8 (5.29)	188.2 (9.89)	424.7 (13.2)	
Site 270 (2014)	11.7 (0.71)	5.82 (0.19)	46.7 (2.48)	54.0 (1.54)	104.6 (4.20)	208.9 (2.94)	666.0
(1993 – 2013)	12.3 (0.17)	6.47 (0.03)	46.2 (1.60)	57.1 (1.74)	108.4 (1.52)	211.6 (3.28)	
Site 268 (2014)	12.0 (2.05)	5.98 (0.11)	68.3 (3.70)	53.7 (4.27)	120.7 (2.68)	245.0 (3.84)	666.0
(1993 – 2013)	13.9 (0.21)	6.51 (0.02)	61.3 (2.09)	60.3 (1.84)	104.6 (4.16)	226.3 (4.81)	

Notes: Cond. = conductivity; ANC = acid-neutralizing capacity; TIS = total inorganic solutes; m amsl = meters above mean sea level.

3.3.6 West Prong of the Little Pigeon River Water Chemistry

Eight sampling locations within the West Prong of the Little Pigeon River (WPLPR) drainage basin (Sites 30, 66, 71, 73, 74, 233, 234 and 237) have been monitored since 1993. Table 9 summarizes mean values of water quality parameters in the current year (2014) and in all prior years. The table is organized to group sites within individual WPLPR reaches, where sites 237, 233, 74 and 73 are in Walker Camp Prong, sites 234 and 71 are in Road Prong, and sites 66 and 30 are in the WPLPR main stem, downstream of the confluence of the other two prongs.

Without exception, mean pH and ANC concentrations in 2014 samples were greater than the overall mean values for all prior years. Stream chemistry in the WPLPR shows strong spatial trends. The clearest trend is seen in the Walker Camp Prong – WPLPR basin; pH and ANC start at levels consistent with severe stream acidification (Site 237: pH < 5; ANC < 0 $\mu\text{eq}/\text{L}$) and increase with distance downstream. The initial acid conditions in this small headwater reach of Walker Camp Prong were in part due to oxidation of reduced-sulfur (pyritic) minerals in Anakeesta Formation bedrock, which is exposed to the atmosphere at several locations throughout this region. The

oxidation of sulfide to sulfate can generate a large amount of acidity as a by-product, resulting in sulfuric acid leaching into soil water and migrating into drainage channels and creeks.

Of special note was the sharp increase in pH and ANC (and in dissolved solids) between Sites 237 and 233. This abrupt shift in stream chemistry is believed to be the result of dolomitic chat that is applied to road surfaces in this watershed during winter driving conditions (NPS, *pers. comm.*). The carbonate mineral content of this road treatment disperses and migrates into the creek system in the Site 233/234 area, and neutralizes the acidity introduced into the creek water from upstream sources. Also note the slight decrease in pH and ANC observed between Site 74 and Site 73. Located between these two sites is the confluence of an unnamed tributary originating from the Alum Cave area of this watershed. The Alum Cave region of the park also has exposed Anakeesta Formation bedrock, which is susceptible to oxidation and formation of acidity, just as at the headwaters of the Walker Camp Prong. The leached sulfuric acid migrates into that unnamed tributary, which mixes at the confluence with the “treated” stream water from Walker Camp Prong. The mixture resulted in a slight depression in pH and ANC, but the effect was localized and is neutralized by the confluence with Road Prong water further downstream.

Similar spatial patterns were seen in the Road Prong – WPLPR basin. Stream pH and ANC go from relatively low values (Site 234: pH 6.1 and ANC ~20 ueq/L) to larger values further downstream (Site 30: pH 6.7 and ANC ~90 ueq/L). Solute concentrations (as reflected in conductivity and TIS data) increase with distance downstream, which is common in watersheds that accrue dissolved solutes from weathering minerals throughout the expanding drainage area. Solutes in Road Prong may not originate from one point-source (e.g., bedrock oxidation at headwaters), but from natural geologic weathering throughout the drainage area. An observation to note for this stream branch was the relatively larger ion charge imbalance in 2013 samples from Sites 71 and 234, as compared to the mean ion charge imbalance in 2013 samples from the other sampling sites in this watershed.

Table 9. Summary of water chemistry data for West Prong of Little Pigeon River sampling sites. Current year and mean of all prior years (standard error of the mean is shown in parentheses). Data organized by river-reach: Walker Camp Prong and Road Prong merge just downstream of Sites 73 and 71, and continue as West Prong of Little Pigeon River.

Sampling Site (Data Years)	Cond. μS/cm	pH	ANC μeq/L	Σ(anions) μeq/L	Σ(cations) μeq/L	TIS μeq/L	Elevation (m amsl)
Walker Camp Prong							
Site 237 (2014)	15.0 (2.31)	4.85 (0.01)	-11.6 (2.18)	111.4 (3.19)	97.7 (7.56)	225.7 (7.92)	1378
(1993 – 2013)	19.8 (0.25)	4.87 (0.03)	-12.6 (0.90)	123.2 (2.20)	80.9 (4.48)	223.7 (6.05)	
Site 233 (2014)	28.5 (2.23)	5.90 (0.05)	91.0 (16.6)	148.8 (9.84)	238.2 (20.8)	480.6 (42.0)	1297
(1993 – 2013)	24.3 (0.35)	6.17 (0.05)	34.4 (2.84)	156.9 (1.82)	151.2 (9.14)	343.4 (11.2)	
Site 74 (2014)	27.5 (1.80)	5.88 (0.07)	108.6 (22.0)	149.8 (8.52)	236.0 (13.3)	497.1 (19.8)	1164
(1993 – 2013)	25.6 (0.43)	6.51 (0.04)	69.1 (3.90)	142.1 (1.84)	164.0 (10.3)	375.6 (12.9)	
Site 73 (2014)	23.8 (1.47)	5.84 (0.05)	60.7 (8.74)	133.2 (2.54)	200.4 (14.4)	397.1 (24.3)	1024
(1993 – 2013)	21.0 (0.33)	6.32 (0.03)	38.4 (2.43)	130.7 (1.91)	130.6 (7.58)	300.6 (9.10)	
Road Prong							
Site 234 (2014)	14.2 (0.59)	5.69 (0.09)	16.5 (0.06)	91.0 (3.42)	108.0 (6.12)	219.7 (10.3)	1524
(1993 – 2013)	15.2 (0.17)	5.89 (0.03)	16.6 (1.17)	100.2 (1.19)	95.8 (4.37)	212.0 (5.17)	
Site 71 (2014)	14.6 (0.71)	5.73 (0.07)	27.6 (2.19)	88.0 (0.81)	120.6 (2.71)	240.0 (5.49)	1037
(1993 – 2013)	16.3 (0.31)	6.19 (0.03)	30.4 (2.18)	98.9 (2.25)	108.0 (5.51)	236.4 (7.30)	
W. Prong Little Pigeon River							
Site 66 (2014)	21.4 (0.84)	5.84 (0.05)	56.0 (4.79)	131.7 (13.8)	180.7 (9.22)	371.4 (26.4)	817
(1993 – 2013)	20.4 (0.38)	6.33 (0.03)	39.4 (1.98)	121.4 (1.53)	129.1 (7.19)	290.9 (8.09)	
Site 30 (2014)	22.5 (0.12)	5.90 (0.06)	91.6 (5.75)	105.9 (4.71)	194.3 (1.20)	394.3 (3.88)	436
(1993 – 2013)	20.9 (0.21)	6.50 (0.03)	63.0 (2.50)	112.3 (1.86)	141.3 (7.40)	314.6 (8.69)	

Notes: Cond. = conductivity; ANC = acid-neutralizing capacity; TIS = total inorganic solutes; m amsl = meters above mean sea level.

3.3.7 Hazel Creek Water Chemistry

Eleven sites (Sites 211, 224, 310, 311, 479, 480, 481, 482, 483, 484 and 485) in Hazel Creek were sampled in 2014 (Table 10). Data for most sites were available back to 1996; Sites 221, 310 and 311 have been monitored since 1993. Table 10 shows mean values of water quality parameters in the current year (2014) and in all prior years. Sites are organized into groups based on reach or tributary: Site 310 is in Bone Valley Creek tributary; Sites 481, 482, 483 and 480 are in a tributary here called Sugar Fork Creek; and Sites 221, 224, 485, 484, 311 and 479 are in the main stem of Hazel Creek.

Stream chemistry was relatively consistent within the drainage basin; differences in the water chemistry parameters vary only slightly among the 11 sampling sites.

Table 10. Summary of water chemistry data for Hazel Creek sampling sites. Current year and mean of all prior years (standard error of the mean is shown in parentheses). Data are organized by river-reach: Bone Valley Creek and Sugar Fork Creek merge into the main stem of Hazel Creek.

Sampling Site (Data Years)	Cond. μS/cm	pH	ANC μeq/L	Σ(anions) μeq/L	Σ(cations) μeq/L	TIS μeq/L	Elevation (m amsl)
Sugar Fork Creek							
Site 481 (2014) (1993 – 2013)	18.0 (n=1)	6.00 (n=1)	77.8 (n=1)	71.6 (n=1)	161.7 (n=1)	313.1 (n=1)	774
	18.3 (0.61)	6.55 (0.04)	86.3 (3.24)	78.3 (4.13)	126.6 (9.23)	289.9 (12.2)	
Site 482 (2014) (1993 – 2013)	14.0 (n=1)	6.22 (n=1)	76.1 (n=1)	204.3 (n=1)*	134.3 (n=1)	415.8 (n=1)	774
	13.8 (0.33)	6.55 (0.04)	89.5 (3.29)	40.4 (0.97)	111.9 (6.82)	240.3 (7.66)	
Site 480 (2014) (1993 – 2013)	14.7 (0.42)	6.16 (0.24)	89.7 (12.4)	45.0 (2.02)	144.6 (13.9)	281.0 (23.4)	707
	14.5 (0.34)	6.59 (0.04)	86.6 (3.22)	47.3 (1.22)	112.0 (6.33)	244.6 (7.91)	
Site 480 (2014) (1993 – 2013)	13.5 (0.38)	6.29 (0.11)	87.1 (13.3)	36.9 (0.29)	137.8 (14.0)	262.8 (26.7)	666
	13.6 (0.36)	6.59 (0.04)	85.3 (2.62)	39.9 (1.97)	105.2 (5.97)	229.2 (7.33)	
Bone Valley Creek							
Site 310 (2014) (1993 – 2013)	12.5 (0.04)	6.24 (0.10)	77.5 (16.4)	40.9 (1.80)	127.0 (7.10)	246.7 (21.4)	683
	12.7 (0.33)	6.56 (0.03)	76.7 (3.04)	41.1 (1.06)	90.2 (5.61)	207.1 (6.85)	
Walker Creek							
Site 485 (2014) (1993 – 2013)	11.9 (0.01)	6.27 (0.10)	72.3 (4.79)	33.1 (1.11)	112.7 (12.1)	219.2 (15.7)	872
	11.3 (0.25)	6.52 (0.04)	71.7 (3.10)	33.9 (1.15)	89.3 (5.13)	193.9 (6.49)	
Hazel Creek							
Site 221 (2014) (1993 – 2013)	10.1 (n=1)	5.98 (n=1)	30.0 (n=1)	50.2 (n=1)	87.4 (n=1)	170.0 (n=1)	1219
	10.5 (0.28)	6.21 (0.04)	28.9 (1.58)	57.7 (2.03)	70.2 (3.92)	157.6 (4.91)	
Site 224 (2014) (1993 – 2013)	10.3 (0.35)	6.17 (0.03)	44.1 (4.74)	41.4 (3.87)	98.7 (3.99)	185.4 (4.76)	1219
	10.4 (0.41)	6.38 (0.35)	42.8 (2.54)	43.8 (2.67)	98.4 (2.62)	183.4 (5.45)	
Site 311 (2014) (1993 – 2013)	11.0 (0.27)	6.21 (0.10)	62.0 (6.84)	36.1 (1.84)	103.8 (3.28)	203.2 (7.99)	754
	10.7 (0.24)	6.46 (0.04)	54.8 (2.62)	38.6 (1.08)	38.6 (1.08)	84.0 (4.44)	
Site 479 (2014) (1993 – 2013)	11.9 (0.33)	6.12 (0.10)	65.5 (10.9)	48.6 (6.27)	115.9 (6.41)	231.8 (22.8)	657
	11.9 (0.27)	6.50 (0.03)	65.7 (2.91)	40.6 (1.78)	88.6 (4.97)	194.3 (5.91)	
Site 479 (2014) (1993 – 2013)	12.5 (n=1)	5.93 (n=1)	62.7 (n=1)	39.4 (n=1)	115.7 (n=1)	220.3 (n=1)	530
	11.7 (0.31)	6.54 (0.04)	68.6 (2.25)	38.1 (1.39)	90.9 (5.31)	198.2 (6.68)	

3.4 Park-Wide Water Chemistry: Toxicological Thresholds

Schwartz et al. (2014) reviewed the literature of aquatic toxicological thresholds for pH, aluminum, and zinc. It is well documented that growth of trout species is inhibited at water pH < 5.5, and trout abundance is reduced at pH < 5.0.

3.5.1 pH

Tennessee and North Carolina State Water Quality Standards for all designated uses (domestic water supply, industrial water supply, fish and aquatic life, recreation, irrigation, and livestock watering and wildlife) specify that water pH shall not fluctuate more than 1.0 unit over a period of 24 hours and shall not be outside the ranges: 6.0 to 9.0 in wadeable streams, and 6.5 to 9.0 in larger rivers, lakes, reservoirs, and wetlands (Tennessee Department of Environment and Conservation [TDEC] General Water Quality Criteria rule 0400-40-03-.03 Criteria for Water Uses, December 2013 revision). In Tennessee, streams are classified as impaired with respect to pH when “10% or more of sample measurements do not meet the numeric water quality criteria.” Given that the basis for the “10%” requires evaluation of multiple years of pH data, it is beyond the scope of this Annual Report. Reported here are counts and samples that did not meet the designated use criterion for pH, not impairment status. The information presented here is useful for assessing stream impairment in other reports. Of the 241 Park-wide samples collected in 2014, 127 samples were non-compliant with the pH criterion (< 6.0). They were collected from sites throughout the GRSM, with no apparent correlation to location or elevation. With two exceptions (Sites 488 and 237), the pH values of all sites appear shifted lower by an average of ~0.4 pH units in 2014 as compared to 2013 and to long-term average pH since 1991 (see Tables 3 through 10). Titration and pH analysis QC results do not indicate an instrumentation or method problem. This systematic shift in pH independent of site or watershed is evident in the long-term stream survey data, particularly in the 2001-2008 time period. Time of year sampled might be a contributing factor; however, a complete explanation for this pH shift is unclear at this time.

3.5.2 Aluminum

The current toxicity threshold for total dissolved aluminum is 0.20 mg/L (Baldigo and Murdoch 1997), but the toxicity of dissolved aluminum may be strongly dependent on speciation (Burns 1989). In 2014, four samples had total aluminum concentrations above the criterion value, and not unexpectedly, they were associated with low pH stream water:

- Site EPLR-4 in Little River (one sample; [aluminum; Al] = 0.23 mg/L)
- Site EPLR-5 in Little River (one sample; [Al] = 0.22 mg/L)
- Site 252 in Oconaluftee Creek (one sample; [Al] = 0.37 mg/L)
- Site 485 in Hazel Creek (one sample; [Al] = 0.31 mg/L)

Curiously, samples from locations with typically lowest pH and historically high total aluminum concentrations (e.g., Walker Camp Prong 237 and 74, and Cosby Creek Site 4 and 137) had aluminum below 0.2 mg/L in 2014 samples. The Oconaluftee Creek Site 252 had the highest aluminum concentration (0.37 mg/L) and one of the lowest pH (4.99), as expected; however, other samples were atypical in 2014. Examples are Site 485 in Hazel Creek with aluminum concentration of 0.31 mg/L but a pH of 6.23, and the two East Prong Little River sites (EPLR-4 and -5) with aluminum above 0.2 mg/L but pH of 5.19 and 5.54, respectively.

3.5.3 Zinc

The current toxicity threshold for total dissolved zinc is 0.219 mg/L (Schwartz et al. 2014). None of the 241 stream survey sites had zinc concentrations above this value.

4.0 Laboratory Data Quality Evaluations

Procedures for chemically analyzing samples for pH, ANC, conductivity, ions, and dissolved metals were based upon approved standard methods (Appendix B). WQ results for all samples are reported and archived in the NPSTORET database; however, data quality is reported here. In 2014, 490 water samples were analyzed: (i) NDW precipitation at OS and TF, soil lysimeter, and SW/NE stream water samples (N = 249) and (ii) Park-wide WQ “Vital Signs” stream water grab samples (N = 241).

Water samples collected in the field were transported to UTK-CEE lab and stored in a walk-in cooler at 2°-6° Celsius (C). Within 48 hours of collection, samples were allowed to equilibrate to room temperature and were analyzed for pH, ANC, and conductivity. The other analyses (i.e., ions and dissolved metals) were performed on the samples within standard holding times. On occasion, the volume of a water sample (e.g., soil lysimeter or precipitation samples during the dry season) was insufficient to process by the normal vacuum filtration procedure. In such cases, the available sample volume was filtered through a pre-rinsed syringe filter cartridge (0.45 µm pore size) directly into corresponding instrument vials and preserved appropriately for the corresponding analysis. Side-by-side checks for potential differences in analytical results between the normal vacuum filtration and the alternate syringe filter method confirmed that both methods yielded equivalent analytical results for the same samples.

The precision and bias of WQ data was inferred based on several QA procedures, standards and reference samples. These include known-concentration QA standard solutions, split sample duplicates, known-addition spiked samples, USGS certified QA solutions, and field, method and instrument blanks. A typical acceptability criterion for precision and bias of spike recovery or blind QA sample analysis is $\pm 20\%$ of target value (Standard Methods 1999). Absence of cross-contamination from laboratory activities was confirmed by analyzing lab deionized water (DIW) in three forms: instrument blanks (1% nitric acid in DIW), method blanks (a 1% nitric acid DIW solution processed as an unknown sample), and field blanks (lab DIW bottled in a field sample bottle, taken to the field during sampling events, and returned to the lab). Analyzing method blanks and instrument blanks provide information on water source purity, labware cleanliness and lab technique. Field blanks provide information on field collection technique and sample handling.

The ability of an analytical instrument or method to accurately and repeatedly detect analytes is an important factor in data quality. A number of indices have been defined to quantify analytical sensitivity (KoeHN and Zimmerman 1990), including limits of detection (LOD; equivalent of the instrument detection limit) and limits of quantitation (LOQ; equivalent to the reporting limit); however, methods for determining these are not entirely standardized (Childress et al. 1999). Methods and calculations by the UTK-CEE lab to obtain LOD and LOQ were based on an approach reported by the USGS (Childress et al. 1999). The LOD can be thought of as “the smallest measured concentration of a substance that can be reliably measured by using a given analytical method” *under ideal conditions* (Timme 1995). The LOQ is based on the LOD, adjusted by a selected “safety factor” (5x) to increase the level of confidence that the reported concentration, obtained under routine lab conditions and random variability, truly represents the concentration in the sample.

This year, the LOD was determined by measuring a QA spiked solution containing known amounts of each analyte. The QA solution was analyzed repeatedly (n replicates), and the mean concentration and standard deviation from the mean were calculated. The LOD for each analyte was calculated as the product of the calculated standard deviation (s) and the Student's t value at {n-1} degrees of freedom and a 99% confidence level ($\alpha = 0.01$):

$$LOD = [s] \cdot [t_{(n-1, 1-\alpha=0.99)}]$$

The LOQ for each analyte was defined as 3 times the LOD.

4.1 Ion Chromatography Data Quality

Samples were analyzed for anions and cation (ammonium) concentrations on a dual-channel IC system consisting of ICS-1100 cation and ICS-2100 anion chromatographs, and an AS-AP autosampler (holding 2-mL sample vials and using 25 μ L injections). Cation peak separation was obtained with a CERS-500 (4 mm) suppressor, guard and analytical columns, with a dilute sulfuric acid eluent (flow rate 1.0 milliliter per minute; mL/min). Anion separation was obtained using an ASRS-300 (4 mm) suppressor, guard and analytical columns, with potassium hydroxide (KOH) eluent (1.0 mL/min) generated internally with an eluent generation cartridge (EGC).

Calibration curves from the instruments had coefficient of determinations (R^2) > 0.9995. Table 11 summarizes the measured analytical limits (LOD and LOQ) for analytes on the IC, the reported precision of replicate field samples, and recovery efficiency of spiked field samples ("matrix spike"). Analytical results from analyses of QA samples by IC were within the acceptance criterion ($\pm 20\%$) in 2014. The mean concentrations of measured ions in processed DIW and field sample blanks were near or slightly above the 2014 LOD and below the 2014 LOQ (Table 11). Precision of replicate analyses was 1.7%, 0.7%, 4.2% and 2.2% for chloride, nitrate, sulfate and ammonium, respectively. Matrix spike recovery efficiency for the anions was between 100% and 101%; recovery efficiency for ammonium was 98%.

Table 4. IC limits of quantitation and QA blank results in milligrams per liter (mg/L).

QA Activity	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	NH ₄ ⁺
Limits of Detection ¹ (N)	0.044 (217)	0.144 (217)	0.108 (217)	0.024 (92)
Limit of Quantitation ¹ (N)	0.132	0.432	0.324	0.072
Mean concentration method blanks ² (N)	0.087 (35)	0.159 (35)	0.191 (217)	0.037 (37)
Mean concentration field blanks ³ (N)	0.081 (31)	< 0.144 (31)	0.249 (31)	< 0.024 (31)
Matrix duplicate precision, % (N)	1.70% (39)	-0.72% (40)	4.25% (40)	2.17% (24)
Matrix spike recovery, % (N)	100.3% (40)	100.6% (40)	100.4% (40)	97.7% (24)

¹ Limit of Detection = (Standard Deviation) x (Student's t @ 99% Confidence Level and sample size, N);
Limit of Quantitation = 3 x Limit of Detection

² Matrix blanks are 1% nitric acid solutions (ultra-pure grade) in Type 1 deionized water, prepared in lab.

³ Field blanks consist of Milli-Q (Type 1) deionized water in sample bottles, carried into the field and exposed to field conditions, and returned to lab to be processed as ordinary samples.

4.2 Inductively Coupled Plasma-Atomic Emission Spectrometry Data Quality

Major cations [sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+})] and six trace elements [aluminum (Al), copper (Cu), iron (Fe), manganese (Mn), silicon (Si), and zinc (Zn)] were analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Standards were prepared using certified ICP reagents (SPEX CertiPrep, Metuchen, NJ) and Milli-Q (Type 1) DI water (EMD MilliPore, Billerica, MA). Standard curves produced by the instrument were checked for linearity (target $R^2 > 0.9999$) prior to sample introduction. The ICP-AES gave highly correlated non-linear detector responses to concentrations of some elements; sodium, potassium and aluminum are reported to respond in this manner.

4.2.1 Quantitation Limits, Lab (Instrument) and Field Blanks

Results of LOD, LOQ and QA matrix blanks are summarized in Table 12. The LOD for the 10 elements ranged from 0.027 to 0.081 milligrams per liter (mg/L), and were within typical ranges for this analytical method. Mean concentrations of elements in QA matrix blank samples were below respective LOD. The results indicate good laboratory technique, control from cross-contamination, and resolution power for 2014. Mean concentrations of elements in field blank samples were below respective LOD. The results indicate good field sample collection technique.

4.2.2 Quality Control Check (QCC) Solutions

A quality control check (QCC) standard solution, matching the low concentration standard, was prepared from certified reagents and Milli-Q (Type 1) DI water, and run every 12 samples to monitor instrument function during each run. The measured QCC concentrations were compared to nominal

Table 5. ICP-AES limits of quantitation and QA blank results in milligrams per liter (mg/L).

Element	Limit of Detection ¹ (N)	Limit of Quantitation ¹ (N)	Mean Concentration Method Blanks ² (N)	Mean Concentration Field Blanks ³ (N)
Aluminum	0.043 (171)	0.130 (171)	< 0.043 (5)	< 0.043 (31)
Calcium	0.060 (174)	0.180 (174)	< 0.060 (5)	< 0.060 (31)
Copper	0.027 (174)	0.081 (174)	< 0.027 (5)	< 0.027 (31)
Iron	0.029 (174)	0.088 (174)	< 0.029 (5)	< 0.029 (31)
Potassium	0.053 (174)	0.158 (174)	< 0.053 (5)	< 0.053 (31)
Magnesium	0.063 (174)	0.190 (174)	< 0.053 (5)	< 0.063 (31)
Manganese	0.033 (174)	0.098 (174)	< 0.033 (5)	< 0.033 (31)
Sodium	0.029 (170)	0.086 (170)	< 0.029 (5)	< 0.029 (31)
Silicon	0.081 (174)	0.243 (174)	< 0.081 (5)	< 0.081 (31)
Zinc	0.059 (135)	0.178 (135)	< 0.059 (5)	< 0.059 (31)

¹ Limit of Detection = (Standard Deviation) x (Student's t @ 99% Confidence Level and sample size, N);
Limit of Quantitation = 3 x Limit of Detection

² Matrix blanks are 1% nitric acid solutions (ultra-pure grade) in Type 1 deionized water, prepared in lab.

³ Field blanks consist of Milli-Q (Type 1) deionized water in sample bottles, carried into the field and exposed to field conditions, and returned to lab to be processed as ordinary samples.

concentrations, as mean % accuracy relative to nominal concentrations (Table 13).

Table 6. ICP-AES accuracy (based on prepared QCC standards)

Element	N	Mean % Accuracy	Standard Error *	CV **
Aluminum	155	99.1 %	0.27 %	3.6 %
Calcium	158	101.4 %	0.19 %	2.5 %
Copper	158	99.5 %	0.17 %	2.3 %
Iron	158	99.0 %	0.18 %	2.3 %
Potassium	158	99.9 %	0.17 %	2.2 %
Magnesium	158	100.4 %	0.20 %	2.7 %
Manganese	158	100.2 %	0.20 %	2.6 %
Sodium	154	100.0 %	0.16 %	2.1 %
Silicon	158	100.4 %	0.25 %	3.3 %
Zinc	117	99.2 %	0.17 %	2.0 %

* Standard Error (%) = 100 x Mean accuracy divided by square-root of number of sample

** Coefficient of Variation (CV; %) = 100 x standard deviation divided by mean accuracy

The bias and precision of QCC analyses had an overall accuracy of 99.9% for all elements combined, and an overall standard error of 0.20%. All 10 elements were measured with similar accuracy (range: 99.0% to 101.4%) and precision (standard error range: 0.17% to 0.27%; coefficient of variation range: 2.0% to 3.6%).

4.2.3 Analytical Precision: Matrix Duplicate Analysis

Analytical precision was evaluated by analyzing duplicate split samples of every 20th sample, and comparing measured concentrations of in each split pairs (Table 14).

Analytical precision had an overall mean difference of < 0.01% for all 10 elements combined, and an

Table 7. ICP-AES method precision and bias (duplicate split samples and spiked samples)

Element	Split Analysis Mean % Difference *	N	Spiked Analysis Mean % Recovery **	N
Aluminum	0.81 % (S.E. = 1.9%)	11	100.0 % (S.E. = 0.8%)	36
Calcium	-0.60 % (S.E. = 0.4%)	34	98.8 % (S.E. = 0.8%)	36
Copper	All Split Samples Near LOD		100.3 % (S.E. = 0.5%)	35
Iron	All Split Samples Near LOD		100.3 % (S.E. = 0.6%)	35
Potassium	0.45 % (S.E. = 0.9%)	34	101.3 % (S.E. = 0.9%)	35
Magnesium	-0.85 % (S.E. = 0.5%)	34	99.8 % (S.E. = 0.8%)	35
Manganese	All Split Samples Near LOD		101.5 % (S.E. = 0.7%)	36
Sodium	0.52 % (S.E. = 0.6%)	31	99.6 % (S.E. = 0.7%)	35
Silicon	-0.28 % (S.E. = 0.1%)	33	99.2 % (S.E. = 0.7%)	35
Zinc	All Split Samples Near LOD		99.2 % (S.E. = 0.6%)	34

* Difference (%) = 100 x (absolute value of replicate results difference / replicate results mean)

** Recovery (%) = 100 x (measured analyte mass divided by the added analyte mass);
S.E. = standard error of the mean

overall standard error of 0.7%. Accurate results were obtained for metal well above their LOD: aluminum (0.81%; N=11); calcium (-0.60%; 34); potassium (0.45%; 34); sodium (0.52%; 31); magnesium (-0.85%; 34); and silicon (-0.28%; 33). In contrast, copper, iron, manganese and zinc in the split sample pairs were near LOD, and were noisy and unrepresentative (shown by “All Split Samples Near LOD”).

4.2.4 Analytical Accuracy: Matrix Spike Analysis

Accuracy (bias) of ICP-AES analyses was assessed by analyzing field samples spiked with known amounts of analyte and calculating percent of added-mass that was detected. Recovery efficiencies of all 2014 spiked-samples (Table 14) averaged 100.0% for all elements combined, with an overall standard error of the mean of 0.7%. Individual metals were measured with similar accuracy; mean % recovery for individual elements ranged from 98.8% to 101.5%.

4.3 USGS QA Reference Samples (Inter-Laboratory Comparison Study)

Certified quality assurance reference samples are obtained each year from USGS as part of a laboratory quality assessment program. The current year and two archived USGS QA reference samples were analyzed periodically during the year. Mean concentrations were calculated and compared to the Most Probable Values (MPV) in the certified USGS QA reference samples (found at <http://bqs.usgs.gov/srs/>). USGS QA samples analyzed this year were:

- T-219, N-123 and P-63 (Fall 2014 round)
- T-217, N-121 and P-62 (Spring 2014 round)
- T-215, N-119 and P-61 (Fall 2013 round)

Samples numbers beginning with “T” are trace element samples and were analyzed for all 10 metals. Sample numbers beginning with “N” are samples with low nutrient concentrations and were analyzed for nitrate (as nitrogen), nitrite (as nitrogen), phosphate (as phosphorus), and ammonium (as nitrogen). Samples numbers beginning with “P” are precipitation samples and analyzed for base cations (sodium, potassium, magnesium and calcium), anions (chloride, sulfate, and phosphate), pH and conductivity. Results from these USGS QA sample analyses are presented as percent deviation from the MPV reported by USGS, in Table 15 for IC analyses and in Table 16 for ICP-AES analyses. Due to oversight, the values reported to USGS for sample T-219 were not corrected for 10-fold dilution during preparation. The corrected concentrations in sample T-219 are reported here.

Accuracy results of IC analysis of USGS QA study samples were within the acceptable criterion of $\pm 20\%$. Analytical accuracy for nitrate was $\leq 2.4\%$; for chloride and sulfate ranged between 0.7% and 8.9%; and for ammonium ranged between 7.9% and 11.4% (Table 15). Accuracy results of ICP-AES analysis of USGS QA study samples were within the acceptable criterion of $\pm 20\%$. Accuracy for all metals combined was 103.1%, 100.9% and 106.2% for T-219, T-217 and T-215, respectively, and 99.9%, 101.2% and 98.7% for P-63, P-62 and P-61, respectively. Accuracy for individual metals was within acceptance criterion of $\pm 20\%$; in fact, all element-specific accuracy were within 10% of the MPV, except for sodium in sample T-215 (112.2% accuracy; N = 19). In all USGS QA reference samples, sodium or potassium were the least accurate (on average) of the measured elements (i.e., had the largest deviation from the MPV).

Table 15. Ion chromatograph blind-sample accuracy QA summary (anions and cations; concentrations in milligrams per liter)

Sample (Year)*	Constituent	Measured (S.E.) # samples	Actual (USGS)	% difference
N-123 (Fall 2014)	NH ₄ ⁺ (as N)	0.267 (0.13%) N=25	0.279	4.2 %
	NO ₃ ⁻ (as N)	0.251 (0.24%) N=3	0.257	2.4%
	NO ₂ ⁻ (as N)	0.395 (0.10%) N=10	0.40	1.2 %
	PO ₄ (as P)	0.185 (0.20%) N=10	0.19	2.4 %
N-121 (Spring 2014)	NH ₄ ⁺ (as N)	0.091 (0.42%) N=27	0.098	7.5 %
	NO ₃ ⁻ (as N)	0.419 (0.49%) N=37	0.418	0.1 %
N-119 (Fall 2013)	NH ₄ ⁺ (as N)	0.218 (1.3%) N=14	0.222	1.7 %
	NO ₃ ⁻ (as N)	0.276 (1.4%) N=7	0.272	1.5 %
P-63 (Fall 2014)	Cl ⁻	5.03 (4.3%) N=12	4.93	1.9 %
	SO ₄ ²⁻	0.452 (0.5%) N=12	0.420	7.6%
P-62 (Spring 2014)	Cl ⁻	2.42 (0.9%) N=50	2.37	2.1 %
	SO ₄ ²⁻	1.82 (0.9%) N=50	1.85	1.6 %
P-61 (Fall 2013)	Cl ⁻	11.8 (33.4%) N=10	11.9	1.0 %
	SO ₄ ²⁻	0.515 (3.6%) N=10	0.49	5.2 %

* Samples consist of current and past-years' USGS Round-Robin reference quality assurance samples. UTK-CEE is designated as "lab #228" in the list of participating labs.

Table 8. Analytical results of blind-sample accuracy QA assessment using USGS certified reference samples. Three T ("trace") and three P ("precipitation") samples were analyzed throughout the year.

Element	T-219 (N=14)	T-217 (N=29)	T-215 (N=19)	P-63 (N=9)	P-62 (N=21)	P-61 (N=8)
Aluminum	102.2% (3.8%)*	88.4% (5.8%)	108.6% (5.3%)	n/a	n/a	n/a
Calcium	101.9% (0.7%)	102.1% (0.6%)	105.2% (0.8%)	99.9% (0.4%)	101.5% (0.5%)	100.3% (1.1%)
Copper	BDL	BDL	BDL	n/a	n/a	n/a
Iron	93.6% (3.6%)	BDL	BDL	n/a	n/a	n/a
Potassium	109.8% (1.2%)	107.4% (0.5%)	107.1% (1.1%)	101.2% (1.8%)	104.7% (0.6%)	109.0% (1.0%)
Magnesium	102.0% (1.1%)	102.3% (0.6%)	102.4% (0.8%)	97.9% (1.9)	102.4% (0.6%)	96.4% (0.6%)
Manganese	101.5% (N=1)	105.3% (0.4%)	BDL	n/a	n/a	n/a
Sodium	98.8% (1.5%)	97.9% (0.5%)	112.2% (0.4%)	100.8% (0.8%)	96.7% (0.3%)	89.0% (0.7%)
Silicon	100.0% (1.6%)	103.4% (0.9%)	101.7% (0.6%)	n/a	n/a	n/a
Zinc	98.3% (N=1)	100.2% (1.7%)	BDL	n/a	n/a	n/a

* Standard Error (%) in parentheses = 100 x standard deviation ÷ square-root of number of samples
n/a = not applicable; BDL = below detection limit for that element

4.4 Ion Charge Balance Check

Data quality checks also include computing the ion charge balance between positively charged (cations) and negatively charged species (anions) in water samples. The ion balance for GRSM water samples was calculated by subtracting concentrations (µeq/L) of base cations, ammonium and proton (positive charge ions) from chloride/nitrate/sulfate and ANC (negative charge ions). USEPA

suggests that a charge balance deviation of $\leq 5\%$ is considered adequate recovery of measured dissolved ionic species; however, low ionic-strength samples are prone to charge balance deviations $> 10\%$ (Fritz 1994; Murray and Wade 1996) due to the large relative error inherent in low-concentration analyses.

The ion balance calculations for 2014 NDW samples are summarized in Table 17. The chemical analyses of NDW samples with substantial concentrations of ions (the two streamlets and the three soil water horizons) gave excellent charge balance results, ranging between -5.2% and +6.4%. Consistent with the caveat reported in the literature, the charge balance deviations in chemical analyses of low-ionic strength precipitation samples (OS and the two types of TF samples) were larger.

Soil water from the shallowest soil horizon (A_w) had (on average) a negative charge balance deviation, indicating the presence of unmeasured or under-reported positive-charge ions in those samples. All other NDW sample types had (on average) positive charge balance deviation, indicating the presence of unmeasured or under-reported negative-charge ions. Unmeasured anions include inorganic species such as fluoride (F^-), phosphate (HPO_4^{2-}) and bicarbonate (HCO_3^-), and dissolved organic carbon (DOC) compounds. Ion chromatograms consistently showed the presence of a ubiquitous bicarbonate ion (from dissolution and dissociation of atmospheric carbon dioxide) and a small amount of fluoride, and occasionally the presence of small unidentified anion peaks. The DOC component consists of ionizable organic compounds of various molecular sizes (e.g., acetate, phenate, tannate, fulvic acids and low-molecular weight humic acids); the degree of DOC ionization is pH-dependent. Since DOC analysis is not part of the current monitoring program, the amount of charge imbalance explained by DOC is unknown. The charge balance deviation in OS samples is likely due to high relative error inherent in low-concentration analyses.

Table 9. Ion charge balance (as mean percent difference between positive and negative charge ions) in Noland Divide watershed water samples (streamlets, precipitation and soil water). Number of samples is shown in parentheses.

Watershed Sample Type	NE Streamlet	SW Streamlet	TF* (buckets)	TF* (funnels)	OS	Soil Water (upper)	Soil Water (middle)	Soil Water (lower)
Annual Mean (N)	+5.1% (21)	+4.7% (22)	+28.1% (18)	+20.2% (9)	+13.9% (13)	-5.2% (10)	+1.4% (8)	+6.4% (6)

* Throughfall (TF) samples collected in buckets for winter samples (November to April) and in jugs attached to funnels for summer samples (May to October).

The sign of the reported values indicate (on average) the direction of deviation. Negative deviation indicates more negative charge measured (insufficient cation concentration); positive deviation indicates more positive charge measured (insufficient anion concentration).

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Appendix A: Algorithm for calculating monthly and annual precipitation volumes and deposition mass for NDW samples

Data Processing Procedure:

1. Open a dataset (in Excel spreadsheet format) containing precipitation sample retrieval dates, precipitation amounts per sample, and ion concentrations (nitrate, sulfate, other) in each precipitation sample.

Note: Precipitation amounts might be in any number of various units; ultimate units must be in cubic centimeters (cm³) of precipitation per square cm (cm²) of collection container opening area (cm³ / cm² = cm depth).

Note: For consistency, the day on which a precipitation samples is retrieved shall not be included in that precipitation sample's collection period. For example, a precipitation sample retrieved from the field on 15 June 2014 is assumed to represent precipitation collected since the previous sample retrieval date up through the previous day, 14 June 2014. The day on which a sample is retrieved (i.e., 15 June 2014) shall be considered part of the next sample retrieval period.

2. Sort the dataset by sample retrieval date, in order of earliest to most recent.
3. Add one row between the spreadsheet's header row and the first row of data.
4. Enter a "dummy" date to the new blank cell in the "Sample Retrieval Date" column. The date should be in the same year and month as the first data entry in the dataset, but an earlier day-of-month (e.g., first day of month).
5. Add 15 new columns to the spreadsheet. It is recommended to add the new columns to the right of the last column of the original dataset spreadsheet. The contents of the 15 columns are listed below (A through M), along with the Excel formulae that calculate the content of the columns.

Note: In the following examples, the formulae are written with the following cell-address defined:

- spreadsheet-row Row #3 contains the cells being calculated or used in calculations
- spreadsheet-column A contains the sample retrieval date,
- spreadsheet-column F contains the raw precipitation data (in centimeters)
- spreadsheet-column J contains the concentration of chemical #1 (in equivalents per liter)
- the 15 inserted columns start at spreadsheet-column AA.

a. Year of sample retrieval date (column AA) =YEAR(\$A3)

b. Month of sample retrieval date (column AB) =MONTH(\$A3)

c. Define “sample collection period” as the number of days between the sample’s retrieval date and the prior sample’s retrieval date.

d. Fraction of the “sample collection period” associated with the current month (the month of the current sample retrieval date) (column AC):

=IF(NOT(MONTH(\$A3)=MONTH(\$A2)),(\$A3-DATE(YEAR(\$A3),MONTH(\$A3),1))/DATEDIF(\$A2,\$A3,"d"),1)

e. Fraction of the “sample collection period” associated with the prior month (the month in which the prior precipitation sample was retrieved) (column AD): =1-AC560

- Note: Infrequently, more than one month will have transpired between the current sample retrieval date and the prior sample retrieval date. In such cases, the “sample collection period” will be more than one month (e.g., > 31 days). The Excel formula calculations should accurately handle such cases.)

f. Adjusted precipitation during time-interval; the precipitation amount (cm) associated with each sample retrieval date (column AE): =(\$AC3* F3)+(\$AD4*F4)

g. Adjusted monthly precipitation; the total precipitation amount (cm) associated with the current month (the month of the current sample retrieval date) (column AF):

=IF(NOT(MONTH(\$A3)=MONTH(\$A4)),SUMIFS(AE:AE,AA:AA,YEAR(\$A3),AB:AB,MONTH(\$A3)), "")

h. Adjusted annual precipitation; the total precipitation amount (cm) associated with the current year (the year of the current sample retrieval date) (column AG):

=IF(NOT(YEAR(\$A3)=YEAR(\$A4)),SUMIF(\$AA:\$AA,YEAR(\$A3),AF:AF), "")

i. Deposition rate (equivalents per hectare per time-interval; eq/ha/interval) of chemical (e.g., sulfur) during time-interval associated with the current sample retrieval date (column AH): =J3*\$F3/10

- j. Adjusted proportional deposition rate (eq/ha/interval) of chemical (e.g., sulfur) = the proportion of the sample's deposition rate associated with the current month (column AI):

$$=($AC3*AH3)+($AD4*AH4)$$

- k. Monthly deposition rate (eq/ha/month) of chemical (e.g., nitrate) associated with the current month (the month of the current sample retrieval date) (column AJ):

$$=IF(NOT(MONTH($A3)=MONTH($A4)),SUMIFS(AI:AI,$AA:$AA, YEAR($A3),$AB:$AB,MONTH($A3)), "")$$

- l. Annual deposition mass of ion (e.g., nitrate); the deposition rate (eq/ha/year) associated with the current year (the year of the current sample retrieval date) (column AK):

$$=IF(NOT(YEAR($A3)=YEAR($A4)),SUMIF($AA:$AA, YEAR($A3),AJ:AJ), "")$$

- m. The each additional set of four columns are merely replication of columns I to L (above), applied to the next chemical of interest (e.g., nitrogen equivalents). The same Excel formulae apply, with appropriate adjustment of cell/row/column addresses.

5. Once the basic calculations in Step 4 are completed, a summary table (in a new spreadsheet page) can be created using the VLOOKUP function in Excel. That summary table will contain: the sample retrieval year (left-most column), sample retrieval month (top header row), monthly totals of precipitation (cm) and deposition rates (eq/ha/yr) or weighted-monthly concentrations (micro-Eq/L) (main body of table), and annual totals of precipitation (cm) and deposition rates (eq/ha/year) or weighted-annual concentrations (micro-Eq/L) (right-most column):

$$=SUMIFS($AG:$AG, $B:$B, $A3, $C:$C, B$2)$$

Spreadsheet cell address definitions:

Original Data:

Excel column A:A	= "Sample Date"	sample retrieval date
Excel column F:F	= "Cum_Precip (cm)"	Precipitation amount (raw data; centimeters)
Excel column J:J	= "Lab Nitrate_IC"	Nitrate concentration (micro-Eq/L)

Excel column K:K	= "Lab Sulfate_IC"	Sulfate concentration (micro-Eq/L)
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Added Columns:

Excel column B:B	= "YR"	year of sample retrieval date (formula "a")
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Excel column C:C	= "MO"	month of sample retrieval date (formula "b")
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Excel column D:D	= "f(currMO)"	proportion (formula "c")
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Excel column E:E	= "f(lastMO)"	proportion (formula "d")
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Excel column AG	= "Adj'd in-Month Precip (cm)"	Precip amount (formula "e")
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Excel column AH	= "Adj'd Monthly Precip (cm)"	Precip amount (formula "f")
-----------------	-------------------------------	-----------------------------

Excel column AI	= "Adj'd Annual Precip (cm)"	Precip amount (formula "g")
-----------------	------------------------------	-----------------------------

Excel column AJ	= "Sulfate Deposition per sample (Eq/ha/intvl)"	(formula "h")
-----------------	---	---------------

Excel column AK	= "Adj'd in-Month SO4 deposition (Eq/ha/intvl)"	(formula "I")
-----------------	---	---------------

Excel column AL	= "Adj'd Monthly SO4 deposition (Eq/ha/MO)"	(formula "j")
-----------------	---	---------------

Excel column AM	= "Adj'd Annual SO4 deposition (Eq/ha/YR)"	(formula "k")
-----------------	--	---------------

Excel column AN	= "T.I.N. Deposition per sample (Eq/ha/intvl)"	(formula "h")
-----------------	--	---------------

Excel column AO	= "Adj'd in-Month T.I.N. deposition (Eq/ha/MO)"	(formula "I")
-----------------	---	---------------

Excel column AP	= "Adj'd Monthly T.I.N. deposition (Eq/ha/MO)"	(formula "j")
-----------------	--	---------------

Excel column AQ	= "Adj'd Annual T.I.N. deposition (Eq/ha/YR)"	(formula "k")
-----------------	---	---------------

Etc... (additional sets of 4 columns (for formulae "h" through "k") should be added to the spreadsheet for each additional analyte or stream water component that is to be calculated).

Appendix B: Methods for Chemistry Analysis Performed at the University of Tennessee –Knoxville.

Analysis	Procedure	Method References
pH (temperature-compensated)	Electrometric	EPA Method 150.1
Specific Conductance (25°C)	Electrometric	EPA Method 120.1
Acid Neutralizing Capacity (ANC)	Automated Titration	Automated Gran Titration for low ionic strength waters, as in Hillman et al. 1986
Anions (NO_3^-, Cl^-, SO_4^{2-})	Ion Chromatography	Standard Methods 4110
Monovalent Cations (NH_4^+)	Ion Chromatography	Modification of Standard Methods 4110
Earth and Trace Metals (Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, & Si)	Inductively Coupled Plasma Spectrophotometer	Standard Methods 3120B EPA Method 6010B EPA Method 3005A

Standard Methods, AWWA (1995).

Appendix C: Site Locations for the Park-wide Stream Water Quality Program.

Site ID	Site Description	Latitude	Longitude	Elevation (m)	Stream Order	Stream System	Survey years (start - end year)
4	Lower Rock Creek	35.7613	-83.2104	634	2	Cosby Creek	1993-
13	Little River at boundary	35.6676	-83.7145	335	5	East Little River	1993-
24	Lower West Prong Little River	35.6568	-83.7102	351	4	West Little River	1993-
30	West Prong Little Pigeon at Headquarters	35.6882	-83.5367	436	4	West Prong Little Pigeon	1993-
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-
114	Cosby Creek at log bridge	35.7486	-83.2007	765	3	Cosby Creek	1993-
137	Upper Rock Creek (Cosby Creek)	35.7462	-83.2163	838	2	Cosby Creek	1993-
138	Inadu Creek (Cosby Creek)	35.7425	-83.227	1058	2	Cosby Creek	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-

Site ID	Site Description	Latitude	Longitude	Elevation (m)	Stream Order	Stream System	Survey years (start - end year)
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-
173	Mill Creek above Abrams Creek	35.591	-83.8536	523	4	Abrams Creek	1993-
174	Abrams Creek below Cades Cove	35.5919	-83.8531	523	4	Abrams Creek	1993-
221	Hazel Creek above cascades	35.5463	-83.5828	1219	2	Hazel Creek	1993-
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-
268	Oconaluftee River below Smokemont	35.5529	-83.3094	666	5	Oconaluftee	1994-
293	Rough Fork at Caldwell House	35.6244	-83.1139	840	3	Cataloochee	1993-
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-
479	Hazel Creek at Campsite 86	35.4723	-83.7193	530	4	Hazel	1996-

Site ID	Site Description	Latitude	Longitude	Elevation (m)	Stream Order	Stream System	Survey years (start - end year)
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-

Appendix D: General Data Quality Assurance Improvements

Several procedures were optimized or instituted beginning this year to support the continuing generation of high-quality analytical data from the UTK-CEE Water Quality Lab.

USGS QA Reference Sample Age

USGS round-robin QA reference sample T-183 was obtained for the Fall 2005 USGS laboratory QA round-robin evaluation. Since that time, this sample has been stored (refrigerated) and used as one of the QA samples for ICP batch analyses. A review of measured concentrations in that sample since early 2006 indicates a possible degradation of that sample over time. The mean concentrations of analytes in that sample no longer match its MPV (Fall 2005). It is plausible that a sample stored, processed and handled for that length of time could degrade in quality.

In response to this finding, a QA policy has been instituted that QA samples (from USGS or any other independent, non-UTK source) will be used for no more than 3 years after its first use.

Beginning this year, the current USGS QA reference samples will be:

- T-215 (Fall 2013), T-217 (Spring 2014) and T-219 (Fall 2014) for ICP trace metals
- P-61 (Fall 2013), P-62 (Spring 2013) and P-63 (Fall 2014) for IC electrolytes and titration parameters
- N-119 (Fall 2013), N-121 (Spring 2014) and N-123 (Fall 2014) for IC nutrients

In each year, use of samples that become older than 3 years will be discontinued, and will be replaced by the most recent USGS QA reference sample. This will provide three years of continuity for the data for any given QA reference sample, and will provide an overlap of two to three years for long-term continuity of analytical QA monitoring. Further, to provide some level of long-term continuity and comparability in reporting the analytical results for QA samples, independent of any particular QA sample, those results will be reported as a relative percentage of the sample's MPV or known concentration. Normalizing the QA results eliminates any data reporting discontinuity associated with differences in concentrations among the QA samples.

Analysis Logsheets

Documentation of analytical work is important for demonstrating data quality, tracking analytical work completed and analysis/sample details, or investigating anomalous results and developing corrective measures. Logsheets were redesigned to consolidate pertinent information previously recorded on numerous individual data sheets. On one, two-sided sheet is contained information on standards source and preparation (traceable back to batch number of primary standards), analysis run specifications (including electronic file name(s) of files generated by instrument's computer software), identification of samples run on that day's batch (including QA samples), QA sample preparation (e.g., spike sample preparation), and space for non-standard information or observations. Duplicate copies of completed logsheets are printed for day-to-day reference, as desired. Original completed logsheets are scanned into "PDF" format and securely stored electronically, and then are archived in secure, project- or analytical instrument-specific binders.

Contamination Prevention / Purity Checks

Several procedures were optimized or instituted to ensure that source water, sample preparation, or labware cleaning procedures are not contributing contamination bias to analytical results.

- Source Water Purity Checks: Samples of Milli-Q™ Type-1 water generated from our in-lab sources will be analyzed periodically to confirm the resistivity indicator values on the water production units.
- Labware Rinse Water Blank Checks: Samples of rinsings collected during labware washing operations will be analyzed periodically to confirm efficiency of wash procedures.
- Method Blank Checks: Periodically, samples of Milli-Q™ Type-1 water generated from in-lab sources will be processed as field samples (i.e., filtered and acidified) and analyzed to confirm the efficiency of sample processing.
- Acid Bath Concentration Checks: Acid-bath water will be analyzed periodically for metals to confirm the efficiency of the acid soaking process for labware.

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

NPS 133/131458, February 2016

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