



Great Smoky Mountains National Park Vital Signs Water Quality Monitoring Program

Annual Report 2015

Natural Resource Data Series NPS/GRSM/NRDS—2016/1035



ON THE COVER

Noland Divide Watershed Study Site

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

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September 2016

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

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

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

This report received informal peer review by subject-matter experts who were not directly involved in the collection, analysis, or reporting of the data. Data in this report were analyzed using standard methods based on established, peer-reviewed protocols and were analyzed within the guidelines of the protocols.

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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 vital signs water quality monitoring program: Annual report 2015. Natural Resource Data Series NPS/GRSM/NRDS—2016/1035. National Park Service, Fort Collins, Colorado.

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Executive Summary

The Great Smoky Mountains National Park (GRSM) 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 data collected for the GRSM monitoring program in 2015. Monitoring data began in 1991 and prior year data summaries can be found in GRSM Annual Reports and journal publications.

NDW precipitation volumes collected during 2015 at the throughfall (TF) and open-site (OS) collection sites were 241 cm and 141 cm, respectively. Mean pH of samples collected at TF and OS sites was 5.18 ± 0.5 and 5.24 ± 0.1 , respectively. Total sulfate deposition at TF for 2015 was 394 equivalents per hectare (eq ha^{-1}), or 18.9 kilograms per hectare ($\text{kg-SO}_4 \text{ ha}^{-1}$). Total inorganic nitrogen (T.I.N.; sum of ammonium & nitrate) deposition at TF was 696 eq ha^{-1} , or $32.0 \text{ kg-TIN ha}^{-1}$. Soil water pH at the NDW monitoring station was 4.53 ± 0.16 , 4.64 ± 0.02 , and 4.63 ± 0.14 , in the upper, middle and lower soil horizons, respectively. The NE and SW streamlets during 2015 had an annual average pH of 5.77 ± 0.02 and 5.97 ± 0.02 , respectively. These streamlets had a mean acid neutralizing capacity (ANC) of 7.3 ± 0.4 and 14.2 ± 0.8 microequivalents per liter ($\mu\text{eq/L}$), respectively.

Of the park-wide stream survey sites monitored in 2015, 35 of the 265 samples had a pH below 6.0 and an ANC below $20 \mu\text{eq/L}$. These samples were collected from sites historically observed to have low pH and ANC stream water, including Double Springs Gap shelter, Cosby-Rock Creek watershed, and Porter-Cannon Creek watershed. Total dissolved aluminum (Al) in only six samples (collected from only three sites) in 2015 was $\geq 0.08 \text{ mg/L}$, a toxicological threshold concentration very near the analytical reporting limit of 0.05 mg/L . These sites are also associated with the lowest measured stream water pH and ANC, consistent with dissolution of aluminum from soils and bedrock minerals. The water pH at Vital Signs stream monitoring sites in 2015 was 6.30 (overall mean; $N = 265$) and ranged between 5.24 and 7.53. A combination of factors in individual GRSM watersheds (i.e., bedrock geology, soil, and vegetation) appears to define the how biogeochemical processes influence the fate and transport of acid deposition pollutants migrating through the soils and entering streams.

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 this 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 ⁻¹ yr ⁻¹	Equivalents per hectare per year
GRSM	Great Smoky Mountain National Park
HDPE	High-density polyethylene
IC	Ion chromatograph or ion chromatography
iCAP-OES	Inductively Coupled Argon Plasma – Optical 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

GRSM's I&M monitoring program, including water quality was revamped in 2014 to reflect knowledge gained from prior studies and new environmental issues, and to standardize it to the NPS-wide Vital Signs Program. In order to address the most critical data needs for individual parks within the constraints of human resources and operating budgets, I&M networks must identify a limited number of *vital signs* that best represent the resource composition, structure, and function of highest interest to individual parks. To effectively develop a monitoring program of vital signs, I&M networks are prioritizing research questions and monitoring data needs related to: (1) focal resources important to each park, which may include individual species, species assemblages, or ecological processes, (2) agents of change or stressors that are known or suspected to cause changes in those focal resources over time; and (3) key properties and processes of ecosystem health (e.g., weather, land use patterns, water quality, soil nutrients).

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

The GRSM Vital Signs Water Quality Monitoring Program consists of (1) periodic baseflow WQ monitoring of designated stream locations (Figure 1) throughout the park (i.e. park-wide stream survey"), and (2) hydrologic and water quality (WQ) sampling and analysis at a monitoring station within the upper Noland Divide watershed (NDW; Figure 2). Monitoring data for 2015 are summarized in this report. Methods used to collect current year monitoring data (i.e. field activities and data collection, laboratory analysis, quality assurance [QA] and management of monitoring data) are included by reference to the GRSM Standard Operating Procedures (SOP) manual (Kulp et al. 2016). The SOP manual, monitoring data, and prior years' GRSM Annual Reports are available online through the IRMA system and associated web sites:

- STORET: http://www3.epa.gov/storet/dw_home.html
- Aquarius: <https://irma.nps.gov/aqwebportal/>
- Data Store: <https://irma.nps.gov/DataStore/>

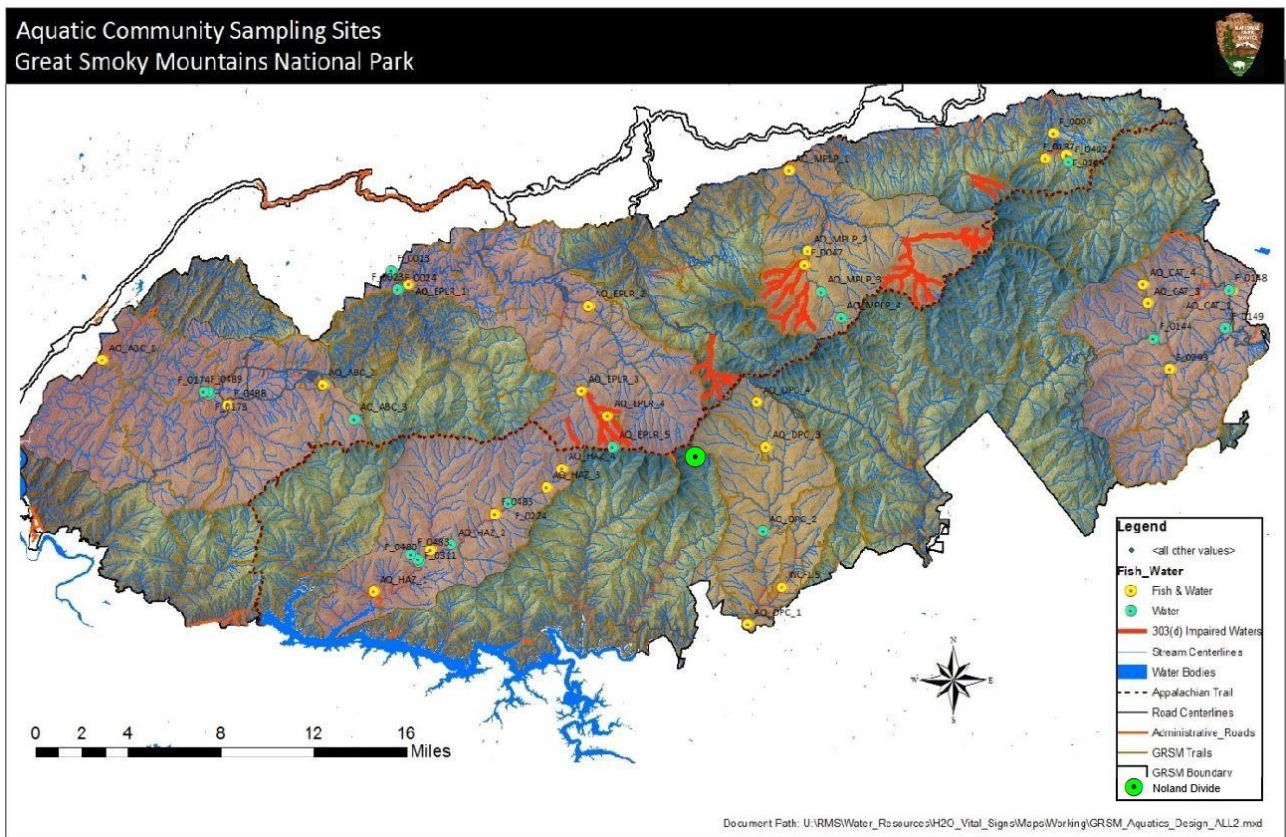


Figure 1. Park-wide water collection sites, Noland Divide watershed (NDW) site, 303(d) listed streams (noted in red), and Vital Signs watersheds shaded in pink/lavender.

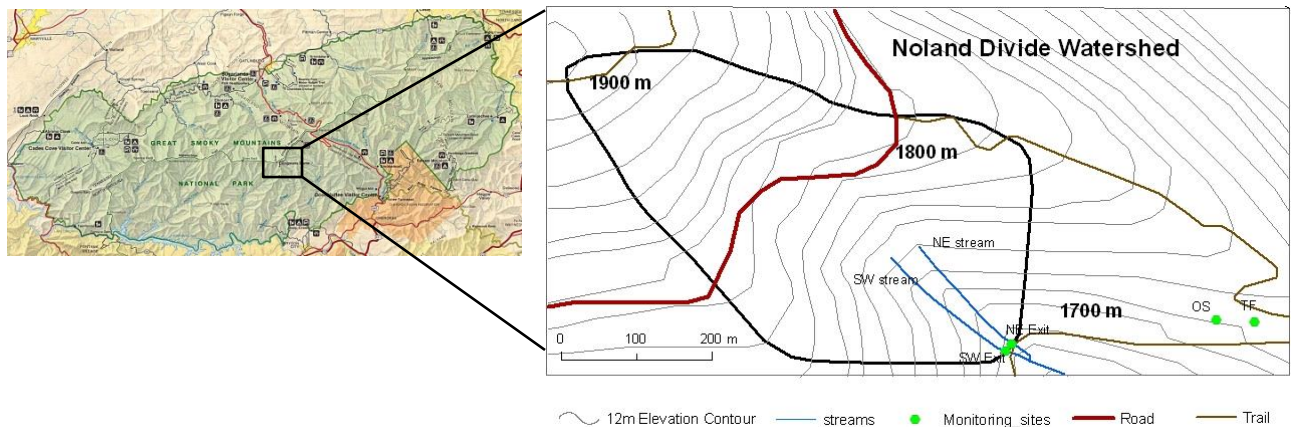


Figure 2. Noland Divide watershed (NDW) showing water quality monitoring stations (OS = open site, TF = throughfall site, SW and NE = streamlet sites).

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; Lindberg and Garten 1988). The ongoing monitoring program at NDW continues to assess effects of stream acidification by providing for a better understanding of 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 have been 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 GRSM (Zhou et al. 2015).

A full suite of continuous monitoring equipment is installed at the NDW site (Figure 2). Hydrology and water quality parameters are monitored at a throughfall (TF) site, an open site (OS), and at two first-order streamlets (northeast [NE] and southwest [SW]). Within the TF site, TF collectors are distributed under the forest canopy, 12 vacuum-operated lysimeters are located in a HDPE manway pit (4 lysimeters per O/A, Bw, and Cb soil horizons), and the site has three soil moisture sensors and an air temperature sensor. The OS site contains a precipitation deposition collector, a standard rain gauge, and a full weather station to record rain intensity, air temperature, barometric pressure, relative humidity, dew point, solar radiation, gust speed, wind speed, and wind direction. H-flume weirs and water quality sondes are installed in both the NE and SW streamlets. Stages are recorded from the two flumes and then converted to discharge. The sondes record pH, conductivity, and temperature. All monitoring equipment and sensors record continuous readings in 15 minute intervals within internal dataloggers. Paper documentation of data and observations in the field are recorded on prepared data forms (see Appendix C) then transcribed to an electronic file.

In addition to continuous monitoring data, water chemistry data were generated from 201 grab samples in 2015. These consisted of: 26 samples each from the NE and SW streamlets; 32 samples from the TF monitoring station; 22 samples from the OS monitoring station; 42, 22 and 31 soil lysimeter water samples from the A, Bw and C soil horizons, respectively, and one composite sample of small water volumes from all three soil horizons.

2.1 Data Quantity/Quality Summary

Table 1 summarizes the data completeness for NDW monitoring activities: precipitation collection (OS), throughfall collection (TF), streamlet water quality parameters (temperature, conductivity and pH) and stage (continuous monitoring in 15-minute intervals). Table 2 summarizes the efficiency with which precipitation was captured by the open-site (OS) monitoring station in 2015.

Table 1. Summary of 2015 data completeness (relative to acceptability criteria) for water quality and quantity, climate parameters, and soil moisture at the Noland Divide watershed monitoring station.

NDW Missing Continuous Monitoring Data Summary							
Parameter	Start		End		Notes	Days Missing	% Missing for Year
	Date	Time	Date	Time			
NE Sonde	2/12/2015	12:45:00	2/14/2015	13:15:00	Low Battery	2.0	0.6%
SW Sonde	2/6/2015	20:45:00	2/7/2015	10:30:00	Low Battery	0.6	2.1%
	2/7/2015	17:30:00	2/8/2015	12:45:00	Low Battery	0.8	
	2/8/2015	14:30:00	2/14/2015	18:00:00	Low Battery	6.1	
NE Stage	2/3/2015	18:11:22	2/14/2015	16:49:34	Dead battery	11.0	8.9%
	3/8/2015	07:18:34	3/16/2015	11:38:19	Dead battery	8.0	
	3/30/2015	12:47:42	4/4/2015	23:59:39	Logger recorded 15 sec instead of 15min. Memory overlapped	5.0	
	4/23/2015	20:18:31	4/27/2015	14:06:49	Logger recorded 15 sec instead of 15min. Memory overlapped	4.0	
	5/7/2015	23:25:34	5/8/2015	13:27:38	Dead battery	0.5	
	5/18/2015	20:48:08	5/22/2015	14:05:22	Dead battery	4.0	
SW Stage	1/1/2015	00:11:17	2/28/2015	13:40:26	Equipment issues, unreliable data	58.0	57.8%
	7/31/2015	23:57:48	11/22/2015	17:45:49	Equipment issues, unreliable data	114.0	
	11/22/2015	17:45:49	12/31/2015	23:59:59	Software unable to connect to device	39.0	
Weather Station	10/23/2015	12:02:00	11/22/2015	16:40:00	Logger failed to launch	29.7	8.1%

http://nadp.isws.illinois.edu/cal/quality_assurance.html

Table 1 (continued). Summary of 2015 data completeness (relative to acceptability criteria) for water quality and quantity, climate parameters, and soil moisture at the Noland Divide watershed monitoring station.

NDW Missing Continuous Monitoring Data Summary							
Parameter	Start		End		Notes	Days Missing	% Missing for Year
	Date	Time	Date	Time			
Throughfall Temp.	2/28/2015	14:39:00	5/22/2015	12:42:00	Logger battery failed due to moisture	82.8	22.7%
Soil Moisture	7/24/2015	7:01:00	7/25/2015	6:31:00	Batteries dead due to short circuit	1.0	12.1%
	7/25/2015	6:31:00	8/3/2015	13:45:00	Battery dead batteries, logger shutdown;	9.6	
	10/23/2015	11:47:00	11/11/2015	15:17:00	Communication failure from probes after first reading of deployment	19.3	
	12/17/2015	8:58:00	12/31/2015	23:59:39	Batteries dead; Software unable to communicate with logger	14.3	

http://nadp.isws.illinois.edu/cal/quality_assurance.html

Table 2. Precipitation capture efficiency (PCE) summary for bi-weekly open-site (OS) monitoring visits in 2015. PCE is the percentage of rain captured by the OS collector compared to the total rainfall during the bi-weekly sampling period. The PCE (Rain Gauge) is calculated by dividing the OS collection by the rain gauge collection. Similarly, the PCE (Weather Station) is calculated by dividing the OS collection by the weather station collection.

Trip Number	Trip Date	OS Collection, inches	Rain Gauge, inches	OS Weather Station, inches	% Collected (Rain Gauge)	% Collected (Weather Station)
1	1/16/2015	0.21	1.13	4.42	18.19%	4.65%
2	2/14/2015	0.65	0.75	5.24	86.13%	12.33%
3	2/28/2015	0.00	2.10	2.18	0.00%	0.00%
4	3/16/2015	3.14	1.27	7.71	247.38%	40.75%
5	3/30/2015	0.44	2.25	2.55	19.57%	17.27%
6	4/13/2015	0.14	1.90	3.26	7.11%	4.14%
7	4/27/2015	5.20	3.60	9.28	144.36%	56.00%
8	5/8/2015	0.50	1.06	0.95	47.09%	52.54%
9	5/22/2015	0.00	1.44	1.3	0.00%	0.00%
10	6/8/2015	0.65	2.12	1.99	30.47%	32.46%
11	6/22/2015	0.79	3.05	3.12	25.99%	25.41%
12	7/6/2015	3.20	5.45	5.72	58.72%	55.95%
13	7/20/2015	0.68	5.14	4.05	13.14%	16.67%
14	8/3/2015	0.00	1.80	1.73	0.00%	0.00%
15	8/17/2015	1.20	1.12	1.81	107.49%	66.51%
16	8/28/2015	2.03	1.98	1.81	102.32%	111.93%
17	9/11/2015	2.85	2.90	2.67	98.20%	106.67%
18	9/25/2015	1.53	1.65	1.68	92.5%	90.88%
19	10/9/2015	5.26	3.55	5.11	148.0%	102.85%
20	10/23/2015	1.44	1.26	1.47	114.2%	97.87%
21	11/11/2015	7.55	6.70	NoData	112.6%	NoData
22	11/22/2015	2.79	1.94	NoData	143.8%	NoData
23	12/5/2015	7.25	3.65	7.19	198.7%	100.87%
24	12/18/2015	2.41	NoData	2.26	NoData	106.53%

Shaded cells indicate conditions on that date included frozen water in rain gauge.

Bold text indicate data collected with the Aerochem Metrics 301 OS Collector

2.2 Continuous Monitoring Meteorological Data

The weather station was installed in 2014 to monitor weather conditions at NDW. The Onset® HOBO® U30 data logger and sensors record rain intensity, temperature, relative humidity, barometric pressure, solar intensity, wind speed, and wind direction every 15 minutes. Table 3 summarizes climate data collected by the weather station instruments in 2015.

Table 3. Summary of monthly mean climate data collected at the Noland Divide Watershed in 2015.

2015 Open Site Weather Station Monthly Averages										
Month	Total Rain, inches	OS Temp, °F	TF Temp, °F	Pressure, inches Hg	RH, %	Dew Point, °F	Solar Rad, W/m ²	Wind Speed, mph	Gust Speed, mph	Wind Dir, ø
January	6.73	29.0	28.7	24.5	77.7	21.4	74.9	0.7	5.6	169.0
February	5.13	24.4	23.8*	24.4	77.0	16.6	99.9	0.6	5.1	165.0
March	10.26	39.9	NoData	24.5	81.9	33.1	95.1	0.4	4.7	179.9
April	12.94	46.0	NoData	24.5	84.3	40.5	109.6	0.5	4.9	191.0
May	3.01	53.8	54.4*	24.7	86.6	49.3	158.3	0.2	2.8	195.5
June	5.42	59.6	58.9	24.6	92.7	57.4	151.5	0.1	2.9	151.5
July	10.03	61.3	60.6	24.6	95.7	60.0	136.1	0.1	2.8	149.9
August	3.63	60.2	59.0	24.6	91.4	57.5	135.4	0.0	1.5	152.8
September	2.66	59.4	55.4	24.7	97.3	58.6	91.4	0.0	0.8	165.8
October*	4.55	49.5	48.5	24.6	77.6	41.0	118.2	0.1	2.4	182.4
November*	2.83	39.5	43.5	24.7	74.6	31.2	72.8	0.2	3.2	192.3
December	16.42	42.9	42.7	24.5	81.6	36.5	56.9	0.8	5.5	200.2
YTD	83.6	47.1	47.0	24.6	84.9	41.9	108.3	0.3	3.5	174.6

Note: Asterisks indicate months with incomplete data. No weather station data from 10/23 – 11/22.

2.3 Continuous Monitoring Stream Data

Year 2015 sonde data for water quality parameters (pH and conductivity) are plotted against discharge (flow in cubic meters per second; $\text{m}^3 \text{s}^{-1}$) for NDW streamlets. Table 4 summarizes the monthly average of stream discharge, pH, conductivity and temperature (Figure 3a) throughout 2015. Figure 3a shows the discharge-pH profile for the NE streamlet for the entire year. Figure 3b shows the discharge-pH profile for the SW streamlet for the entire year. Operational issues and equipment malfunctions caused some SW discharge data to be unreliable. Regression analysis was used to estimate missing discharge values.

Table 4. Mean monthly values of water quality parameters and discharge in NE and SW streamlets at the NDW monitoring station for 2015.

Month	Northeast (NE)				Southwest (SW)			
	Discharge cfs	pH	Spec.Cond $\mu\text{S}/\text{cm}$	Temp. $^{\circ}\text{C}$	Discharge cfs	pH	Spec.Cond $\mu\text{S}/\text{cm}$	Temp. $^{\circ}\text{C}$
January	0.20	6.0	10.9	2.6	0.20	6.0	10.3	2.9
February	0.10	6.0	10.9	1.7	0.12	6.0	10.5	1.7
March	0.40	6.0	10.8	3.8	0.39	6.0	9.9	3.5
April	0.61	6.0	10.7	6.3	0.42	6.1	9.5	6.0
May	0.02	6.1	10.7	8.9	0.05	6.3	9.6	8.6
June	0.02	6.1	10.8	11.4	0.05	6.4	9.7	10.8
July	0.19	5.9	10.7	11.1	0.23	6.1	9.1	10.7
August	0.02	5.9	10.7	11.8	0.04	6.2	9.4	11.2
September	0.03	5.9	10.7	11.2	0.05	6.2	9.8	10.7
October	0.14	6.0	11.1	8.9	0.16	6.1	9.7	9.0
November	0.26	6.0	10.9	7.0	0.26	6.1	9.6	7.4
December	0.41	5.8	10.6	6.4	0.37	6.0	9.5	6.6
Year	0.18	6.0	10.8	7.7	0.20	6.1	9.7	7.6

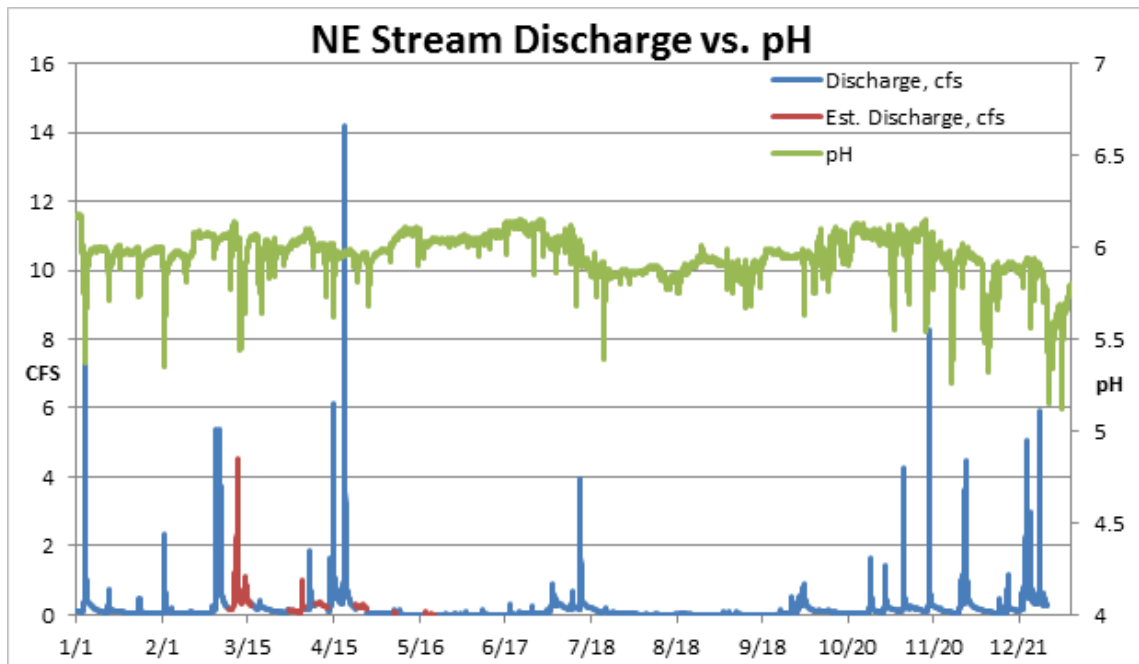


Figure 3a. Stream discharge versus stream water pH, at the northeast (NE) streamlet (2015 sonde data).

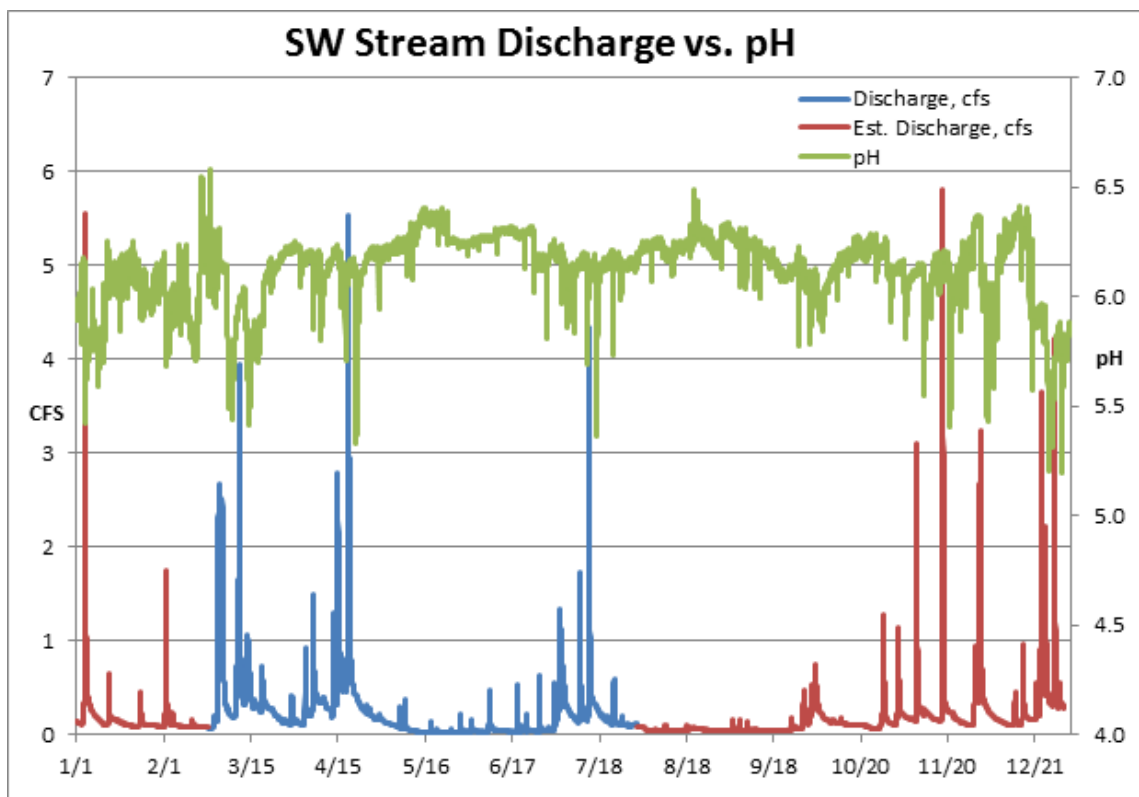


Figure 3b. Stream discharge versus stream water pH, at the southwest (SW) streamlet (2015 sonde data).

2.4 Continuous Monitoring Soil Moisture Data

Soil moisture at the NDW monitoring station was measured continuously by three in-place soil moisture probes within a 2m diameter circle of soil. Table 5 summarizes the monthly average of soil moisture throughout 2015. Figure 4 shows the raw data time profile of soil moisture throughout 2015.

Table 5. Monthly mean soil moisture content, m³/m³, for 2015 at the Noland Divide site. The SM-3 sensor failed during Aug. and Sept. Therefore no data is available for that period.

Probe	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
SM-1	0.437	0.427	0.442	0.443	0.431	0.436	0.443	0.435	0.436	0.445	0.446	0.447	0.438
SM-2	0.381	0.378	0.398	0.395	0.376	0.383	0.393	0.374	0.371	0.384	0.387	0.391	0.384
SM-3	0.37	0.369	0.392	0.386	0.356	0.359	0.375	0.352	-	-	0.378	0.387	0.373

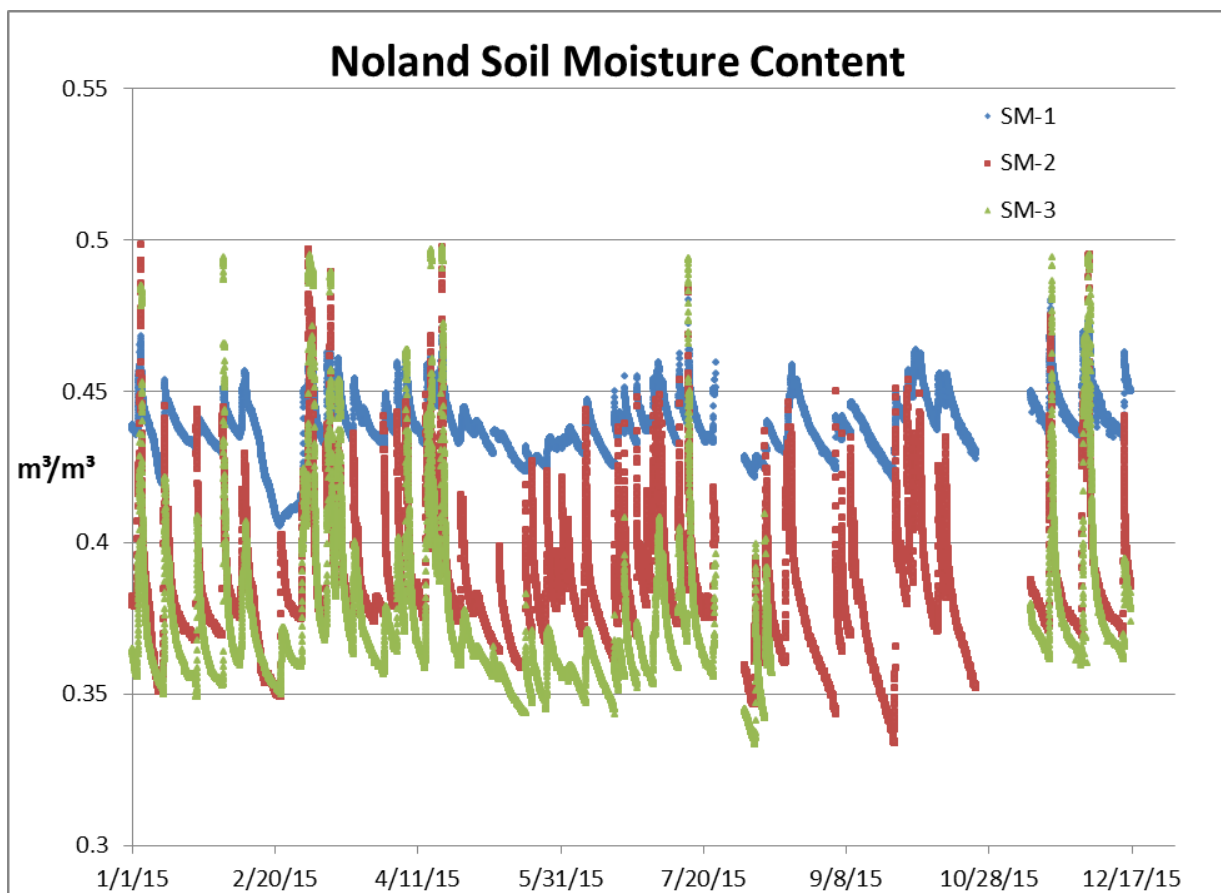


Figure 4. Soil moisture content at the NDW monitoring station for 2015.

2.5 Precipitation (Grab Sample) Data (Quantity and Chemistry)

Table 6 summarizes the annual statistics for precipitation quantity and water quality parameters for OS and TF. Parameters shown are precipitation volume (in centimeters; cm), pH, acid neutralizing capacity (ANC) in units of micro-equivalents per liter ($\mu\text{eq L}^{-1}$). It also summarizes the annual volume-weighted mean values of water quality parameters for OS and TF, in $\mu\text{eq L}^{-1}$. Parameters shown are: major anions (chloride, nitrate, sulfate), ammonium, total inorganic nitrogen (nitrate plus ammonium), and base cations (sodium, potassium, magnesium and calcium). Individual monthly values are tabulated and included as an attachment to this report.

Table 6. Water quantity and quality statistics for open site (OS) and throughfall (TF) precipitation samples collected in 2015. Data for water quality parameters and volume-weighted concentrations are shown as mean $\pm$ standard error (SE) of the mean (and the range of 2015 data in parentheses). Volume-weighted concentrations (microequivalents per liter) of ions in precipitation samples. Data shown are mean $\pm$ standard error of the mean (with range of values in parentheses).

Parameter	Open Site (OS)	Throughfall (TF)
pH	5.24 $\pm$ 0.05 (4.72 – 5.72)	5.18 $\pm$ 0.50 (4.43 – 5.94)
Conductivity ¹	6.7 $\pm$ 0.8 (2.8 – 14.6)	20.5 $\pm$ 2.5 (7.2 – 38.9)
ANC	-6.3 $\pm$ 1.0 (-20.6 – 5.5)	-7.5 $\pm$ 2.7 (-37.5 – 32.8)
Year Total Volume (cm)	141	241
Chloride	2.0 $\pm$ 0.3 (0.5 – 5.7)	22.3 $\pm$ 3.6 (4.0 – 60.8)
Nitrate	5.2 $\pm$ 0.8 (1.3 – 12.5)	21.9 $\pm$ 5.0 (0.6 – 92.1)
Sulfate	6.8 $\pm$ 1.1 (1.6 – 16.5)	18.5 $\pm$ 3.3 (3.6 – 57.4)
Ammonium	3.7 $\pm$ 0.8 (0.04 – 9.8)	14.4 $\pm$ 3.4 (0.01 – 61.9)
T.I.N. ²	9.0 $\pm$ 5.7 (1.5 – 116.1)	36.4 $\pm$ 47.9 (20.9 – 1,115.1)
Sodium	2.8 $\pm$ 0.3 (0.6 – 5.2)	15.4 $\pm$ 1.9 (5.0 – 38.4)
Potassium	1.7 $\pm$ 0.5 (0.3 – 8.2)	38.5 $\pm$ 6.2 (7.8 – 104.0)
Magnesium	1.3 $\pm$ 0.2 (0.4 – 4.1)	13.8 $\pm$ 1.5 (4.4 – 27.0)
Calcium	3.5 $\pm$ 0.5 (1.0 – 9.7)	31.4 $\pm$ 3.2 (10.6 – 56.4)
Base Cations	9.3 $\pm$ 4.1 (4.4 – 74.9)	99.0 $\pm$ 164.4 (1.4 – 2,907.0)
Base Cation Surplus	-4.8 $\pm$ 1.4 (-15.1 – 5.2)	36.3 $\pm$ 9.8 (-40.8 – 114.2)

¹ Conductivity in micro-seimens per centimeter ($\mu\text{S/cm}$); Acid-neutralizing capacity (ANC) and ion concentrations in micro-equivalents per liter (μeqL^{-1})

² T.I.N. = “total inorganic nitrogen” = sum of ammonium and nitrate

2.6 Stream Water Chemistry

Table 7 summarizes the water chemistry data for NE and SW streamlet grab samples from the NDW monitoring station. Values shown are the mean and standard error (SE) of the mean, and the range of data values in parentheses.

Table 7. 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. Values shown are mean $\pm$ standard error (SE) of the mean (and the range of 2015 values in parentheses). Concentrations (microequivalents per liter) of ions in stream water samples. Data shown are mean $\pm$ standard error of the mean (range of values in parentheses).

Parameter	Northeast (NE)	Southwest (SW)
pH	5.77 $\pm$ 0.02 (5.60 – 5.88)	5.97 $\pm$ 0.02 (5.78 – 6.13)
Conductivity ¹	12.8 $\pm$ 0.1 (12.0 – 14.7)	11.6 $\pm$ 0.1 (10.8 – 14.0)
ANC	7.3 $\pm$ 0.4 (2.8 – 13.1)	14.2 $\pm$ 0.8 (8.1 – 22.7)
Chloride	11.2 $\pm$ 0.4 (8.8 – 17.2)	8.5 $\pm$ 0.3 (6.5 – 16.1)
Nitrate	19.0 $\pm$ 0.3 (15.7 – 21.8)	17.2 $\pm$ 0.6 (13.9 – 28.6)
Sulfate	40.3 $\pm$ 0.7 (31.9 – 46.8)	32.1 $\pm$ 0.6 (24.2 – 37.4)
Ammonium	10.3 $\pm$ 2.8 (0.01 – 35.8)	9.7 $\pm$ 2.7 (0.01 – 34.6)
T.I.N. ²	29.3 $\pm$ 3.0 (15.7 – 57.5)	27.0 $\pm$ 3.2 (13.9 – 63.2)
Sodium	25.2 $\pm$ 0.5 (20.7 – 29.9)	23.8 $\pm$ 0.3 (20.0 – 27.4)
Potassium	9.4 $\pm$ 0.3 (7.6 – 13.9)	6.6 $\pm$ 0.2 (5.0 – 9.8)
Magnesium	17.0 $\pm$ 0.1 (15.6 – 19.5)	16.1 $\pm$ 0.3 (14.9 – 23.9)
Calcium	42.7 $\pm$ 0.5 (39.0 – 50.2)	40.6 $\pm$ 0.9 (36.1 – 60.5)
Base Cations (BC)	94.3 $\pm$ 1.5 (82.9 – 113.5)	87.1 $\pm$ 1.7 (76.0 – 121.7)

¹ Conductivity in micro-seimens per centimeter ($\mu\text{S}/\text{cm}$); Acid-neutralizing capacity (ANC) and ion concentrations in micro-equivalents per liter (μeqL^{-1})

² T.I.N. = “total inorganic nitrogen” = sum of ammonium and nitrate

Figures 5 through 8 are scatterplots of NDW streamlet chemistry for current year grab samples: pH (standard units) (Figure 5), ANC ($\mu\text{eq L}^{-1}$) (Figure 6), nitrate ($\mu\text{eq L}^{-1}$) (Figure 7), and sulfate ($\mu\text{eq L}^{-1}$) (Figure 8).

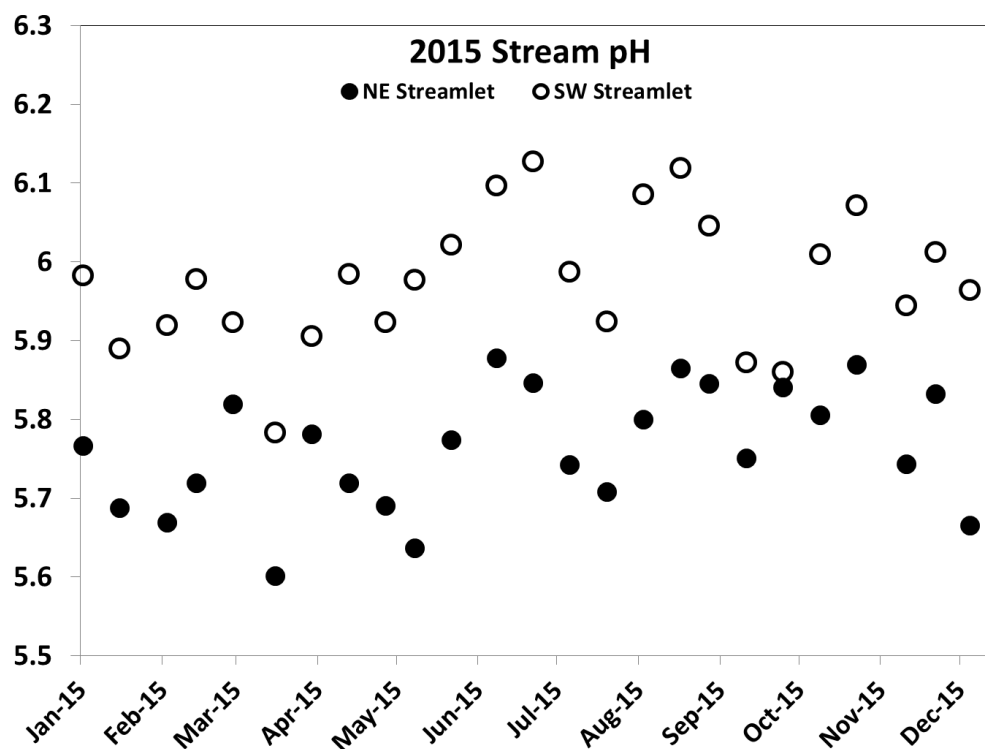


Figure 5. NDW streamlet pH data for 2015 (standard pH units).

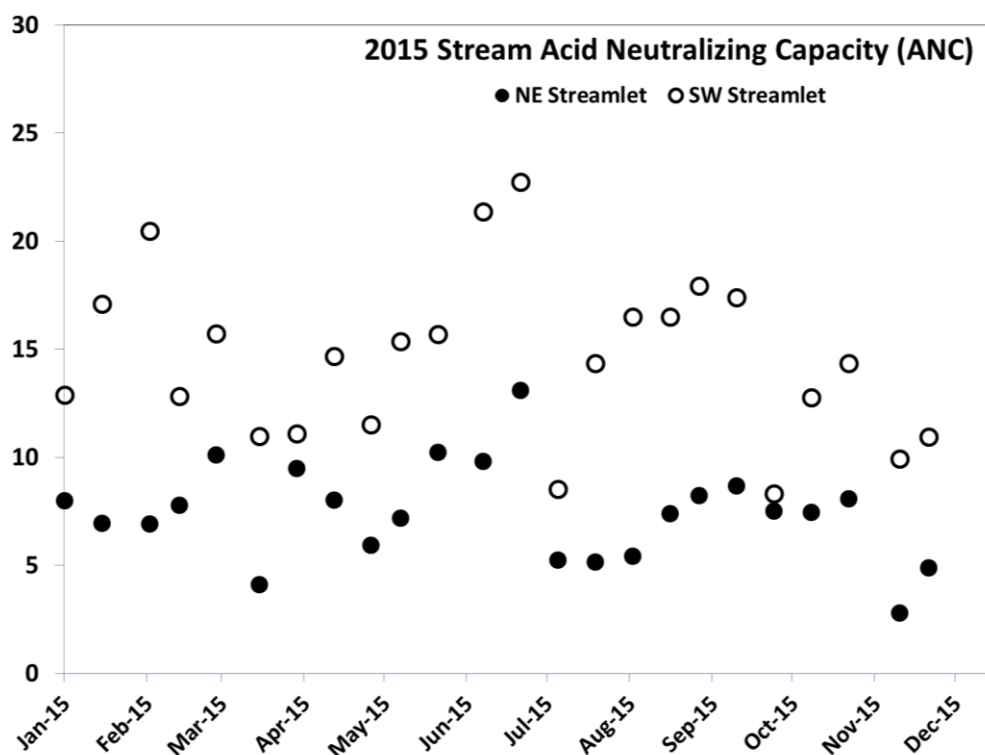


Figure 6. NDW streamlet acid-neutralizing capacity (ANC) data for 2015 (micro-equivalents per liter; $\mu\text{eq L}^{-1}$).

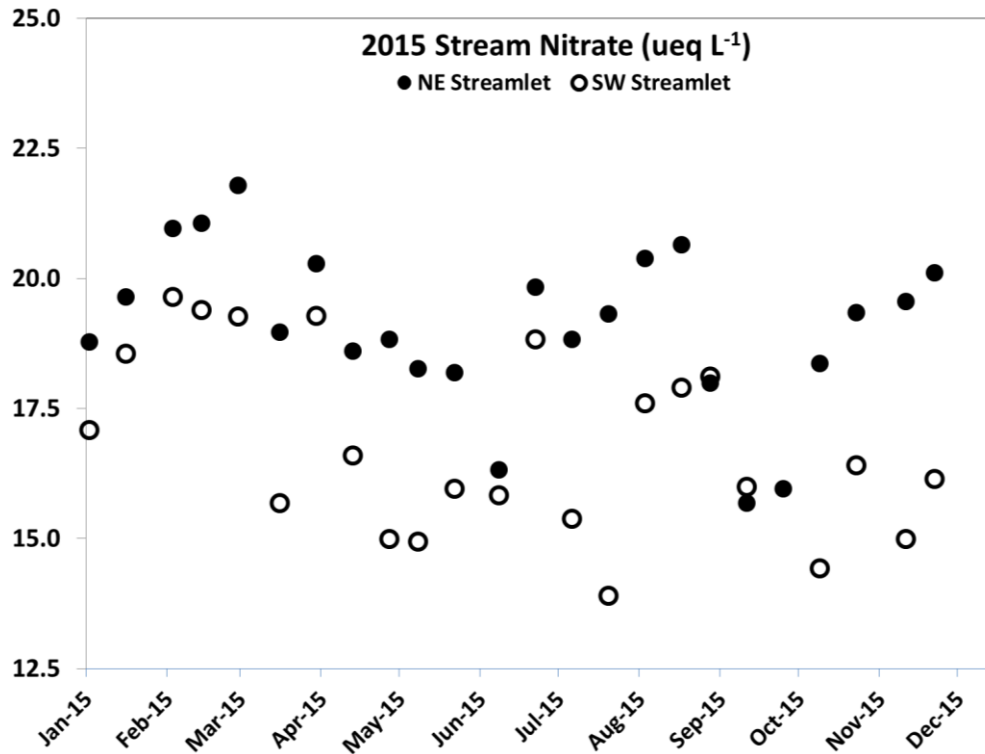


Figure 7. NDW streamlet nitrate concentration data for 2015 (micro-equivalents per liter; $\mu\text{eq L}^{-1}$).

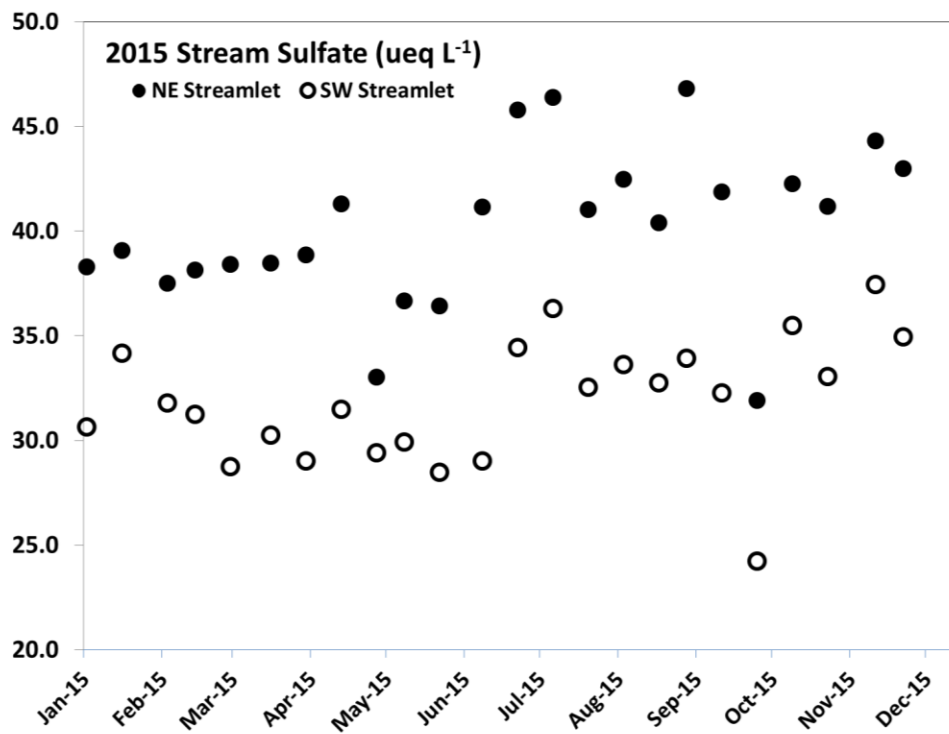


Figure 8. NDW streamlet sulfate concentration data for 2015 (micro-equivalents per liter; $\mu\text{eq L}^{-1}$).

2.7 Soil Water Chemistry

Soil water chemistry of samples collected in 2015 is summarized in Table 8. Samples were collected bi-weekly from lysimeters placed at three horizon depths: A horizon at 8 cm (upper); B_w horizon at 35 cm (middle); and C_b horizon at 65 cm (lower). Total soil water volumes collected were 28.3 liters (L), 6.4 L, and 21.0 L from the upper, middle, and lower lysimeters, respectively.

Table 8. Summary data statistics for conductivity, pH, common anions and base cations in soil lysimeter samples collected in 2015. Values shown are mean $\pm$ standard error (SE) of the mean (and the range of 2015 values in parentheses). Also included are calculated values of sum of base cations (BC), calcium to aluminum molar ratio (Ca:Al), and BC to aluminum molar ratio (BC:Al). Concentrations (microequivalents per liter) of ions in soil water (lysimeter) samples. Data shown are mean $\pm$ standard error of the mean (range of values in parentheses).

Parameter	Upper = A horizon (413)	Middle = B _w horizon (414)	Lower = C _b horizon (415)
pH	4.53 $\pm$ 0.16 (4.25 – 4.70)	4.64 $\pm$ 0.02 (4.42 – 4.85)	4.63 $\pm$ 0.14 (4.50 – 4.76)
Conductivity ¹	24.4 $\pm$ 1.1 (17.1 – 50.5)	23.9 $\pm$ 1.3 (16.6 – 40.3)	23.4 $\pm$ 0.8 (18.9 – 28.3)
ANC	-39.6 $\pm$ 1.8 (-75.4 – -23.3)	-35.0 $\pm$ 2.0 (-59.3 – -19.8)	-35.2 $\pm$ 1.5 (-47.7 – -23.5)
Chloride	13.8 $\pm$ 1.7 (6.1 – 63.6)	16.6 $\pm$ 2.6 (5.7 – 58.7)	9.6 $\pm$ 1.1 (4.4 – 32.1)
Nitrate	46.9 $\pm$ 4.1 (4.3 – 116.5)	47.6 $\pm$ 6.2 (8.2 – 115.2)	57.1 $\pm$ 3.4 (20.5 – 85.0)
Sulfate	43.2 $\pm$ 2.7 (13.0 – 86.0)	49.4 $\pm$ 3.5 (30.2 – 100.7)	37.1 $\pm$ 3.5 (0.00 – 117.2)
Ammonium	6.9 $\pm$ 1.3 (0.01 – 29.8)	8.8 $\pm$ 2.3 (0.01 – 33.4)	7.1 $\pm$ 1.2 (0.01 – 18.3)
T.I.N. ²	53.9 $\pm$ 5.0 (4.7 – 146.3)	56.5 $\pm$ 8.2 (8.6 – 144.5)	64.1 $\pm$ 3.7 (24.4 – 93.7)
Sodium	16.1 $\pm$ 1.0 (10.0 – 36.7)	17.9 $\pm$ 1.7 (9.7 – 48.3)	12.9 $\pm$ 0.7 (0.5 – 18.2)
Potassium	7.1 $\pm$ 0.7 (3.0 – 19.7)	7.9 $\pm$ 0.8 (4.3 – 21.7)	7.8 $\pm$ 0.04 (0.0 – 12.3)
Magnesium	15.3 $\pm$ 0.9 (9.6 – 29.5)	19.0 $\pm$ 2.1 (12.5 – 55.7)	16.3 $\pm$ 0.8 (0.0 – 20.9)
Calcium	12.7 $\pm$ 0.9 (8.0 – 34.7)	12.6 $\pm$ 1.2 (8.0 – 32.0)	17.0 $\pm$ 0.9 (0.0 – 23.2)
Base Cations (BC)	37.2 $\pm$ 2.3 (22.0 – 74.4)	41.7 $\pm$ 4.0 (29.9 – 113.9)	37.3 $\pm$ 1.8 (0.5 – 46.6)
Ca:Al ratio ³	0.3 $\pm$ 0.01 (0.2 – 0.5)	0.2 $\pm$ 0.01 (0.1 – 0.2)	0.3 $\pm$ 0.01 (0.2 – 0.4)
BC:Al ⁴	1.5 $\pm$ 0.1 (1.1 – 3.1)	1.2 $\pm$ 0.1 (0.8 – 1.7)	1.3 $\pm$ 0.05 (1.0 – 1.7)

¹ Conductivity in micro-seimens per centimeter ($\mu\text{S}/\text{cm}$); Acid-neutralizing capacity (ANC) and ion concentrations in micro-equivalents per liter (μeqL^{-1})

² T.I.N. = “total inorganic nitrogen” = sum of ammonium and nitrate

³ Ca:Al = molar ratio of calcium-to-aluminum

⁴ BC:Al = molar ratio of total base cations-to-aluminum

2.8 Atmospheric Deposition Loading

Measured deposition load (kilograms per hectare) data for OS and TF are summarized in Tables 9 and 10, respectively; includes major anions (chloride, nitrate, sulfate), ammonium, total inorganic nitrogen (nitrate plus ammonium), and base cations (sodium, potassium, magnesium and calcium).

Table 9. Summary of deposition load (kilograms per hectare; kg ha⁻¹) from open site (OS) precipitation samples collected in 2015. Deposition values shown are total annual and monthly deposition.

Open Site (OS) (kg ha ⁻¹)													
Parameter	2015	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Chloride	0.97	0.006	0.036	0.100	0.141	0.052	0.052	0.072	0.033	0.183	0.105	0.074	0.122
Nitrate	4.18	0.094	0.647	0.169	0.698	0.319	0.287	0.271	0.466	0.452	0.179	0.243	0.351
Sulfate	4.35	0.055	0.711	0.241	0.550	0.520	0.221	0.301	0.365	0.449	0.239	0.243	0.457
Ammonium	0.89	0.020	0.022	0.057	0.071	0.202	0.046	0.026	0.112	0.147	0.003	0.003	0.182
T.I.N. ¹	5.07	0.114	0.669	0.227	0.769	0.521	0.333	0.297	0.578	0.600	0.182	0.246	0.533
Sodium	0.91	0.007	0.068	0.123	0.085	0.045	0.044	0.091	0.041	0.108	0.094	0.098	0.108
Potassium	0.98	0.006	0.042	0.061	0.065	0.151	0.041	0.044	0.016	0.033	0.446	0.031	0.042
Magnesium	0.26	0.003	0.016	0.010	0.028	0.027	0.013	0.018	0.010	0.015	0.094	0.015	0.013
Calcium	0.99	0.020	0.115	0.031	0.171	0.122	0.048	0.096	0.067	0.083	0.128	0.066	0.048
Sum of B.C. ²	3.15	0.036	0.241	0.225	0.349	0.345	0.146	0.249	0.134	0.240	0.761	0.211	0.211
Protons	0.08	0.0011	0.0116	0.0078	0.0100	0.0042	0.0058	0.0040	0.0056	0.0057	0.0053	0.0104	0.0121

¹ T.I.N = Total Inorganic Nitrogen = Nitrate + Ammonium

² Sum of B.C. = Sodium + Potassium + Magnesium + Calcium

Table 10. Summary of deposition load (kilograms per hectare; kg ha⁻¹) from TF precipitation samples collected in 2015. Deposition values shown are total annual and monthly deposition.

Throughfall (TF) (kg ha ⁻¹)													
Parameter	2015	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Chloride	14.41	0.447	1.139	1.499	1.088	0.779	2.446	1.024	0.499	1.435	1.605	1.115	1.334
Nitrate	27.36	1.398	6.757	5.593	2.733	2.412	2.167	0.948	0.555	1.435	0.073	0.835	2.453
Sulfate	18.92	1.731	4.350	4.715	1.227	1.200	1.109	0.861	0.453	0.667	0.403	1.369	0.830
Ammonium	4.59	0.423	0.692	0.955	0.754	0.505	0.192	0.142	0.487	0.254	0.043	0.000	0.143
T.I.N. ¹	31.95	1.821	7.449	6.548	3.487	2.917	2.359	1.091	1.043	1.690	0.115	0.835	2.596
Sodium	7.31	0.581	0.782	1.107	0.830	0.237	1.134	0.562	0.234	0.264	0.296	0.498	0.789
Potassium	26.38	1.099	0.999	1.263	0.978	0.735	3.243	2.654	1.483	3.943	5.404	3.648	0.935
Magnesium	3.30	0.160	0.401	0.451	0.276	0.104	0.336	0.263	0.171	0.298	0.319	0.333	0.190
Calcium	12.61	0.656	1.528	1.770	1.653	0.376	1.264	0.951	0.671	0.980	0.971	1.151	0.641
Sum of B.C. ²	49.61	2.496	3.710	4.591	3.737	1.452	5.976	4.429	2.560	5.485	6.991	5.630	2.555
Protons	0.28	0.042	0.064	0.074	0.023	0.003	0.007	0.010	0.002	0.002	0.003	0.024	0.021

¹ T.I.N = Total Inorganic Nitrogen = Nitrate + Ammonium

² Sum of B.C. = Sodium + Potassium + Magnesium + Calcium

2.9 Annual Ion Input-Export Budgets

The flux of ions in water passing through the NDW was evaluated with an input-export budget, with input of dissolved ions assumed to come from throughfall throughout the year, and export of dissolved ions assumed to be carried out of the NDW drainage area (17.4 ha) in stream water from the NE and SW streamlets. Continuous stage-discharge monitoring data (Section 2.3) and grab-sample chemical analysis results (Section 2.5) were combined in a more detailed mass-balance analysis to determine the total mass of key ions entering and leaving the NDW. Differences can indicate the current status of the NDW drainage area with respect to net retention or net release of ion species. Sources of potential error in these estimates include precipitation volume capture efficiency, continuous monitoring equipment, extrapolation of grab-sample chemistry results to continuous (15-min increment) stream discharge data, and normal analytical random error.

Figure 9 depicts the quantities of ions entering (throughfall input) and leaving (total stream export) the NDW, in equivalents per hectare over the entire calendar year. Anions (chloride, nitrate and sulfate) and cations (ammonium, sodium, potassium, magnesium and calcium) are shown; total inorganic nitrogen is depicted as the sum of ammonium and nitrate quantities. Throughfall (input) quantities greater than stream export quantities indicate net increase in ion mass within the drainage area; the converse indicates net decrease in ion mass.

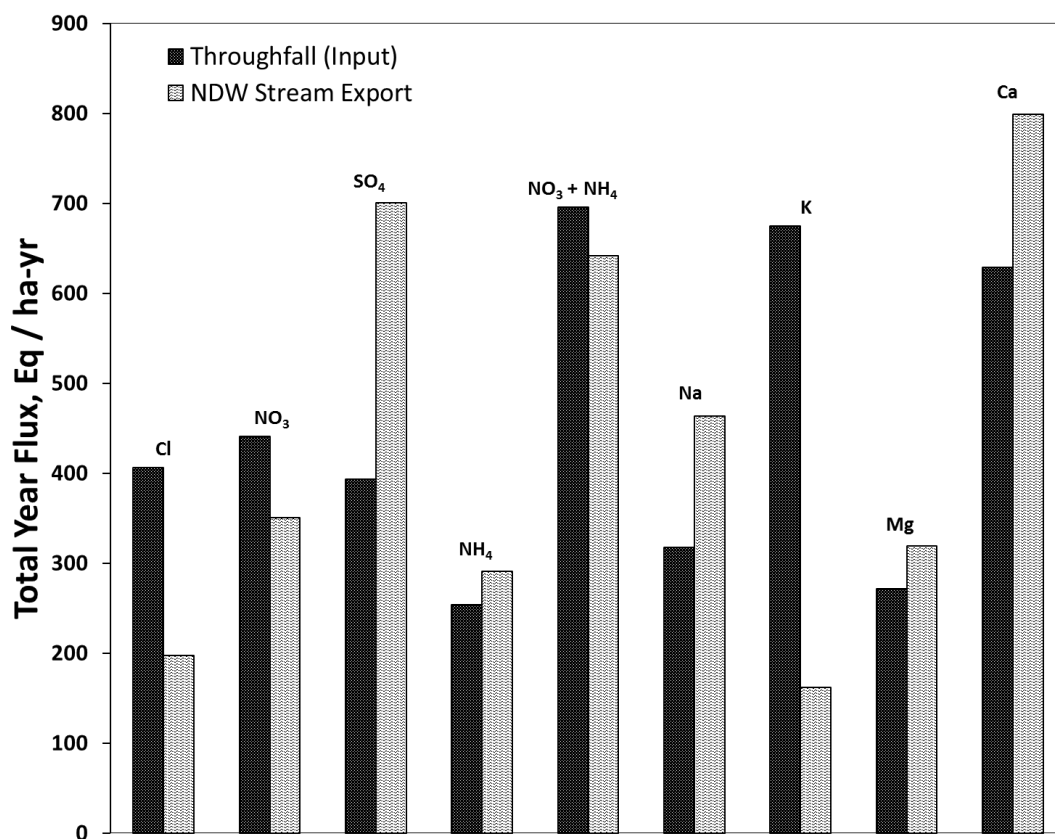


Figure 9. Input-export budget for key ions in the Noland Divide Watershed in 2015. Quantities are given as equivalents per hectare (eq ha^{-1}) over the entire calendar year.

3.0 Vital Signs Stream Survey

Park-wide stream survey (also termed long-term synoptic stream WQ monitoring) began in October 1993 (Schwartz et al. 2014). Currently active sampling sites are distributed among seven watersheds identified by their predominant surface water body (Figure 1): Sample site numbers are summarized in Appendix B. Abrams Creek main stem (3 sites); tributaries to Abrams Creek (4); Cataloochee Creek (8); Cosby Creek (4); Deep Creek (5); Hazel Creek (12); East Prong Little River (8); and Middle Prong Little Pigeon River (5). In 2015, 207 samples from these 49 sampling sites, plus 27 field replicates, were collected and analyzed. Statistics over the period of record were calculated for: pH (standard unit), conductivity ($\mu\text{S}/\text{cm}$), acid-neutralizing capacity ANC ($\mu\text{eq L}^{-1}$), major anions ($\mu\text{eq L}^{-1}$; chloride, nitrate, sulfate), base cations ($\mu\text{eq/L}$; sodium, potassium, magnesium and calcium).

3.1 Vital Signs Water Chemistry: Watershed Summary

Summary statistics were calculated for the seven monitored watersheds and for the individual sites included in the current monitoring program. The results are presented in Table 11.

3.1.1 Abrams Creek Water Chemistry

Abrams Creek WQ data were collected at seven stream sites. Sites 173 and 488 are associated with the Mill Creek tributary to Abrams Creek. Sites 174 and 489 are associated with the main stem of Abrams Creek. Data for these four sites are available back to the beginning of the monitoring program (1993). Sites 156, 200 and 423 were added in 2014. Water chemistry of the seven Abrams Creek sites are markedly different from all other watersheds monitored as part of this GRSM Vital Signs Program, and there are further differences in water quality among individual Abrams Creek sites. Table 12 summarizes the mean $\pm$ standard error (plus range of measured values) for 2015.

3.1.2 Cataloochee Creek Water Chemistry

Cataloochee Creek WQ data were collected at eight stream sites: Sites 129, 130, 144, 147, 148, 149, 293 and 493). Table 13 summarizes the mean $\pm$ standard error (plus range of measured values) for 2015. The sites are presented in sequence from upstream to downstream.

Table 11. Summary of Park-wide stream water chemistry in 2015, organized by watershed. Values shown are mean $\pm$ standard error of the mean (plus range of values in parentheses). The Abrams Creek sites are divided into two subsets: the main stem of Abrams Creek, and tributaries to Abrams Creek.

Parameter	Abrams ³	Abrams tributaries	Cataloochee	Cosby Creek	Deep Creek	Hazel Creek	Little River	Pigeon River
pH	7.08 $\pm$ 0.07 (6.41 – 7.53)	6.28 $\pm$ 0.06 (5.73 – 6.79)	6.34 $\pm$ 0.03 (5.99 – 6.71)	5.95 $\pm$ 0.04 (5.62 – 6.26)	6.42 $\pm$ 0.04 (6.09 – 6.64)	6.32 $\pm$ 0.03 (6.03 – 6.46)	6.26 $\pm$ 0.06 (5.24 – 6.83)	5.90 $\pm$ 0.08 (5.38 – 6.48)
Conductivity ¹	78.3 $\pm$ 8.0 (30.3 – 144.3)	13.8 $\pm$ 0.4 (11.6 – 19.8)	14.6 $\pm$ 0.5 (6.6 – 21.8)	16.2 $\pm$ 0.3 (13.7 – 18.4)	13.6 $\pm$ 0.3 (11.6 – 15.6)	12.4 $\pm$ 0.4 (8.8 – 16.5)	17.4 $\pm$ 0.7 (11.1 – 29.5)	17.0 $\pm$ 1.0 (11.5 – 24.0)
ANC ²	740 $\pm$ 84 (220 – 1,430)	59.4 $\pm$ 7.1 (15.0 – 145.1)	67.6 $\pm$ 4.3 (29.5 – 161.1)	19.7 $\pm$ 2.2 (5.9 – 44.9)	50.9 $\pm$ 4.1 (26.8 – 80.2)	57.6 $\pm$ 4.3 (21.9 – 90.7)	72.6 $\pm$ 8.7 (-11.5 – 236.3)	14.7 $\pm$ 4.7 (-4.6 – 64.4)
Chloride	15.2 $\pm$ 0.5 (11.6 – 19.2)	11.9 $\pm$ 0.4 (8.8 – 16.9)	13.6 $\pm$ 2.3 (8.8 – 116.6)	9.3 $\pm$ 0.3 (7.4 – 15.5)	10.5 $\pm$ 0.4 (8.5 – 14.0)	10.8 $\pm$ 0.2 (9.1 – 12.7)	18.4 $\pm$ 2.6 (9.3 – 97.0)	12.7 $\pm$ 1.7 (7.3 – 29.8)
Nitrate	6.5 $\pm$ 0.7 (0.2 – 10.3)	15.4 $\pm$ 1.6 (4.2 – 31.1)	10.0 $\pm$ 0.8 (0.0 – 20.7)	40.8 $\pm$ 1.2 (25.6 – 49.2)	11.5 $\pm$ 2.8 (0.1 – 31.3)	7.5 $\pm$ 1.3 (1.0 – 19.9)	12.2 $\pm$ 1.9 (0.6 – 56.6)	33.4 $\pm$ 3.5 (14.5 – 54.4)
Sulfate	47.0 $\pm$ 2.5 (33.4 – 72.9)	25.5 $\pm$ 1.1 (19.6 – 47.3)	19.7 $\pm$ 0.5 (13.9 – 27.2)	42.5 $\pm$ 0.8 (35.0 – 49.9)	23.8 $\pm$ 2.5 (11.1 – 46.2)	16.9 $\pm$ 1.0 (8.2 – 27.4)	34.3 $\pm$ 1.5 (20.9 – 86.3)	58.9 $\pm$ 5.3 (32.8 – 102.2)
Sodium	50.2 $\pm$ 1.5 (37.8 – 61.0)	37.2 $\pm$ 1.4 (26.5 – 50.9)	46.6 $\pm$ 1.7 (32.2 – 84.2)	32.7 $\pm$ 1.0 (25.6 – 44.5)	40.0 $\pm$ 1.5 (32.6 – 51.1)	41.2 $\pm$ 1.6 (27.0 – 53.4)	47.4 $\pm$ 3.5 (28.3 – 153.4)	32.7 $\pm$ 2.8 (22.0 – 59.7)
Potassium	15.6 $\pm$ 0.6 (12.6 – 20.1)	10.9 $\pm$ 0.2 (9.4 – 14.1)	13.2 $\pm$ 0.4 (9.5 – 23.5)	9.8 $\pm$ 0.2 (7.5 – 12.4)	10.7 $\pm$ 0.6 (7.1 – 15.7)	10.6 $\pm$ 0.4 (7.9 – 14.5)	14.1 $\pm$ 0.7 (9.1 – 34.5)	7.1 $\pm$ 0.6 (3.6 – 10.3)
Magnesium	149.6 $\pm$ 15.0 (60.9 – 282.3)	22.1 $\pm$ 1.8 (13.9 – 54.5)	23.5 $\pm$ 1.0 (14.9 – 36.9)	31.0 $\pm$ 1.3 (19.5 – 42.6)	21.8 $\pm$ 0.8 (16.5 – 27.2)	22.5 $\pm$ 1.5 (14.5 – 40.4)	29.9 $\pm$ 2.3 (15.6 – 79.8)	37.1 $\pm$ 3.6 (17.6 – 59.7)
Calcium	617 $\pm$ 81 (167 – 1,332)	43.5 $\pm$ 2.2 (32.3 – 85.4)	46.7 $\pm$ 2.0 (29.5 – 79.5)	59.0 $\pm$ 1.8 (46.9 – 78.2)	42.0 $\pm$ 1.8 (27.9 – 54.1)	37.6 $\pm$ 1.9 (24.0 – 55.3)	59.0 $\pm$ 4.0 (29.1 – 148.5)	56.8 $\pm$ 4.0 (33.7 – 84.0)
Base Cations	832 $\pm$ 97 (279 – 1,695)	113.7 $\pm$ 4.9 (87.3 – 202.9)	130.7 $\pm$ 5.2 (88.3 – 219.4)	132.5 $\pm$ 4.1 (102.8 – 175.5)	114.5 $\pm$ 2.8 (98.8 – 136.0)	112.0 $\pm$ 5.1 (74.0 – 161.1)	152.3 $\pm$ 7.8 (86.3 – 302.3)	133.8 $\pm$ 9.3 (84.5 – 211.9)

¹ Conductivity in micro-seimens per centimeter ($\mu\text{S}/\text{cm}$); concentrations in micro-equivalents per liter (μeqL^{-1})

² Acid-neutralizing capacity (ANC) was added to this project's analytical suite in 2005

³ Site 156 (added to monitoring program in 2014) has water chemistry that is intermediate to that of the main stem Abrams Creek sites (174 and 489) and of Abrams Creek tributary sites (173, 488, 200, 423). It is included with the main stem sites for convenience, but that causes the statistics for that subset to be biased low.

Table 12. Summary of Abrams Creek stream water chemistry in 2015. Values shown are mean $\pm$ standard error of the mean (plus range of values in parentheses). Abrams Creek sites are grouped into subsets: main stem Abrams Creek (Sites 174, 489 and 156), Mill Creek tributary (Sites 173 and 488), and Anthony Creek tributary (Sites 200 and 423).

Parameter	Main Stem sites			Mill Creek tributary		Anthony Creek tributary	
	Site 174	Site 489	Site 156	Site 173	Site 488	Site 200	Site 423
pH	7.20 $\pm$ 0.11 (6.87 – 7.53)	7.12 $\pm$ 0.12 (6.74 – 7.49)	6.92 $\pm$ 0.11 (6.41 – 7.22)	6.39 $\pm$ 0.10 (6.12 – 6.79)	6.02 $\pm$ 0.10 (5.73 – 6.29)	6.46 $\pm$ 0.09 (6.24 – 6.75)	6.25 $\pm$ 0.09 (5.91 – 6.47)
Conductivity ¹	92.1 $\pm$ 14.3 (59.0 – 144.3)	92.4 $\pm$ 13.1 (62.3 – 139.2)	50.6 $\pm$ 7.2 (30.3 – 73.3)	12.6 $\pm$ 0.1 (12.2 – 13.1)	13.3 $\pm$ 0.7 (11.6 – 16.7)	15.5 $\pm$ 1.0 (13.5 – 19.8)	13.7 $\pm$ 0.3 (13.0 – 14.8)
ANC ²	897 $\pm$ 152 (531 – 1,430)	854 $\pm$ 136 (517 – 1,366)	470 $\pm$ 94 (220 – 746)	61.5 $\pm$ 9.7 (42.5 – 95.5)	24.6 $\pm$ 5.0 (15.0 – 42.4)	94.0 $\pm$ 14.4 (60.1 – 145.1)	57.6 $\pm$ 10.4 (32.4 – 97.3)
Chloride	15.6 $\pm$ 0.9 (13.5 – 19.1)	15.8 $\pm$ 0.9 (14.1 – 19.2)	14.1 $\pm$ 0.8 (11.6 – 17.2)	12.0 $\pm$ 0.4 (10.5 – 13.1)	10.9 $\pm$ 1.0 (8.8 – 15.2)	11.8 $\pm$ 0.5 (10.7 – 13.4)	13.0 $\pm$ 0.9 (11.1 – 16.9)
Nitrate	8.2 $\pm$ 0.4 (6.7 – 9.9)	8.6 $\pm$ 0.6 (6.6 – 10.3)	2.8 $\pm$ 0.9 (0.2 – 6.7)	10.8 $\pm$ 1.3 (6.6 – 15.7)	26.2 $\pm$ 1.6 (21.1 – 31.1)	6.8 $\pm$ 0.6 (4.2 – 8.7)	17.9 $\pm$ 0.8 (14.0 – 19.7)
Sulfate	50.7 $\pm$ 4.7 (43.2 – 72.9)	49.9 $\pm$ 4.4 (42.9 – 70.6)	40.4 $\pm$ 2.9 (33.4 – 53.1)	26.1 $\pm$ 4.3 (20.5 – 47.3)	25.8 $\pm$ 0.8 (23.7 – 28.6)	23.2 $\pm$ 1.0 (19.6 – 27.0)	26.9 $\pm$ 1.0 (23.8 – 30.7)
Sodium	50.9 $\pm$ 2.3 (45.1 – 61.0)	52.4 $\pm$ 2.5 (45.5 – 60.9)	47.3 $\pm$ 2.9 (37.8 – 57.5)	37.8 $\pm$ 2.2 (31.5 – 47.1)	31.1 $\pm$ 2.2 (26.5 – 40.7)	39.9 $\pm$ 2.7 (32.7 – 50.9)	39.9 $\pm$ 2.6 (34.9 – 49.6)
Potassium	15.3 $\pm$ 1.1 (12.6 – 19.9)	15.9 $\pm$ 1.0 (12.9 – 20.1)	15.4 $\pm$ 1.0 (13.0 – 18.4)	10.2 $\pm$ 0.2 (9.4 – 11.0)	10.4 $\pm$ 0.4 (9.5 – 11.6)	11.3 $\pm$ 0.5 (9.6 – 12.8)	11.8 $\pm$ 0.5 (10.5 – 14.1)
Magnesium	175.9 $\pm$ 27.0 (113 – 282)	174.2 $\pm$ 24.4 (114.0 – 270.7)	98.6 $\pm$ 13.5 (61 – 156)	20.0 $\pm$ 0.6 (17.9 – 21.8)	15.7 $\pm$ 0.5 (13.9 – 17.9)	34.2 $\pm$ 4.3 (25.2 – 54.5)	18.4 $\pm$ 0.5 (17.5 – 20.8)
Calcium	764 $\pm$ 145 (436 – 1,332)	753 $\pm$ 133 (438 – 1,271)	334 $\pm$ 61 (167 – 597)	36.7 $\pm$ 1.2 (32.3 – 41.4)	39.6 $\pm$ 0.9 (37.0 – 43.1)	56.0 $\pm$ 6.3 (42.3 – 85.4)	41.9 $\pm$ 1.2 (39.2 – 46.9)
Base Cations	1,006 $\pm$ 176 (607 – 1,695)	995 $\pm$ 160 (610 – 1,623)	496 $\pm$ 77 (279 – 828)	104.6 $\pm$ 3.8 (91.9 – 119.9)	96.7 $\pm$ 2.9 (87.3 – 105.8)	141.4 $\pm$ 13.4 (111.0 – 202.9)	112.1 $\pm$ 4.1 (104.1 – 128.9)

¹ Conductivity in micro-seimens per centimeter ($\mu\text{S}/\text{cm}$); concentrations in micro-equivalents per liter (μeqL^{-1})

² Acid-neutralizing capacity (ANC) was added to this project's analytical suite in 2005

³ Site 156 (added to monitoring program in 2014) has water chemistry that is intermediate to that of the main stem Abrams Creek sites (174 and 489) and of Abrams Creek tributary sites (173, 488, 200, 423). It is included with the main stem sites for convenience, but that causes the statistics for that subset to be biased low.

Table 13. Summary of Cataloochee stream water chemistry in 2015. Values shown are mean $\pm$ standard error of the mean (plus range of values in parentheses).

Parameter	Site 129	Site 130	Site 144	Site 147	Site 148	Site 149	Site 293	Site 493
pH	6.18 $\pm$ 0.04 (6.04 – 6.30)	6.18 $\pm$ 0.05 (5.99 – 6.26)	6.33 $\pm$ 0.04 (6.14 – 6.39)	6.39 $\pm$ 0.08 (6.09 – 6.56)	6.47 $\pm$ 0.09 (6.19 – 6.71)	6.46 $\pm$ 0.08 (6.17 – 6.62)	6.47 $\pm$ 0.07 (6.20 – 6.65)	6.28 $\pm$ 0.05 (6.14 – 6.38)
Conductivity ¹	12.3 $\pm$ 0.3 (11.4 – 13.2)	12.0 $\pm$ 0.3 (11.0 – 12.8)	13.0 $\pm$ 0.9 (10.8 – 17.0)	15.4 $\pm$ 1.0 (11.0 – 18.2)	18.5 $\pm$ 1.2 (14.5 – 21.8)	16.4 $\pm$ 0.4 (14.9 – 17.1)	16.4 $\pm$ 2.0 (6.6 – 20.3)	12.8 $\pm$ 0.5 (11.7 – 14.6)
ANC ²	39.9 $\pm$ 2.3 (31.4 – 43.8)	38.1 $\pm$ 4.1 (29.5 – 51.1)	63.7 $\pm$ 11.0 (40.2 – 116.7)	75.2 $\pm$ 8.5 (49.0 – 101.4)	103.2 $\pm$ 16.7 (58.4 – 161.1)	80.8 $\pm$ 7.0 (62.2 – 94.3)	82.2 $\pm$ 6.5 (63.0 – 105.6)	58.1 $\pm$ 6.5 (42.0 – 78.3)
Chloride	28.6 $\pm$ 17.6 (9.8 – 116.6)	12.5 $\pm$ 0.7 (10.9 – 14.6)	10.8 $\pm$ 0.6 (8.8 – 12.6)	11.2 $\pm$ 0.7 (9.0 – 13.8)	10.9 $\pm$ 0.5 (9.5 – 13.1)	11.7 $\pm$ 0.7 (9.8 – 13.5)	11.8 $\pm$ 0.6 (10.5 – 14.3)	10.1 $\pm$ 0.5 (8.8 – 11.8)
Nitrate	13.9 $\pm$ 0.6 (11.9 – 16.4)	14.8 $\pm$ 0.7 (12.5 – 17.0)	5.6 $\pm$ 1.2 (0.85 – 8.9)	7.8 $\pm$ 1.7 (3.0 – 12.8)	3.6 $\pm$ 1.7 (0.02 – 9.5)	8.7 $\pm$ 1.0 (6.3 – 12.1)	17.9 $\pm$ 1.0 (13.9 – 20.7)	7.0 $\pm$ 0.5 (5.8 – 8.5)
Sulfate	18.6 $\pm$ 1.6 (14.9 – 24.3)	18.5 $\pm$ 0.7 (16.1 – 21.2)	18.1 $\pm$ 1.1 (14.1 – 21.2)	20.1 $\pm$ 1.3 (16.7 – 25.7)	19.8 $\pm$ 1.4 (16.4 – 25.6)	20.6 $\pm$ 1.0 (18.9 – 24.5)	24.3 $\pm$ 0.7 (21.9 – 27.2)	17.0 $\pm$ 0.9 (13.9 – 19.2)
Sodium	37.4 $\pm$ 1.9 (34.0 – 46.3)	36.5 $\pm$ 2.1 (32.7 – 46.5)	41.5 $\pm$ 4.1 (32.2 – 59.2)	48.3 $\pm$ 4.0 (33.6 – 61.6)	63.4 $\pm$ 5.4 (45.0 – 84.2)	51.2 $\pm$ 3.0 (44.5 – 60.4)	54.1 $\pm$ 2.9 (47.5 – 65.4)	40.6 $\pm$ 2.9 (35.5 – 50.4)
Potassium	11.1 $\pm$ 0.2 (10.1 – 11.8)	10.1 $\pm$ 0.2 (9.5 – 10.9)	12.6 $\pm$ 0.9 (9.7 – 15.0)	14.5 $\pm$ 1.1 (10.8 – 17.2)	16.9 $\pm$ 1.7 (13.2 – 23.5)	15.2 $\pm$ 1.0 (12.5 – 18.3)	13.7 $\pm$ 0.6 (11.9 – 15.4)	11.8 $\pm$ 0.7 (10.1 – 13.6)
Magnesium	18.3 $\pm$ 0.9 (15.6 – 21.8)	17.1 $\pm$ 0.6 (15.8 – 19.7)	19.2 $\pm$ 1.6 (15.3 – 26.3)	25.1 $\pm$ 2.2 (14.9 – 30.3)	30.8 $\pm$ 2.1 (23.4 – 36.9)	27.1 $\pm$ 1.2 (23.3 – 29.8)	31.8 $\pm$ 0.9 (29.0 – 35.3)	18.6 $\pm$ 1.1 (16.2 – 22.3)
Calcium	35.3 $\pm$ 1.7 (30.5 – 40.7)	33.5 $\pm$ 1.3 (29.5 – 37.6)	40.6 $\pm$ 3.5 (30.7 – 54.4)	48.7 $\pm$ 4.3 (31.0 – 60.1)	64.6 $\pm$ 5.9 (43.4 – 79.5)	52.7 $\pm$ 3.3 (42.9 – 60.0)	58.7 $\pm$ 2.2 (51.7 – 65.7)	39.2 $\pm$ 3.0 (33.0 – 48.7)
Base Cations	102.0 $\pm$ 4.4 (93.0 – 120.0)	97.2 $\pm$ 3.7 (88.7 – 113.2)	114.0 $\pm$ 9.8 (88.3 – 155.0)	136.5 $\pm$ 11.4 (90.3 – 168.4)	175.7 $\pm$ 14.5 (125.7 – 219.4)	146.2 $\pm$ 7.9 (124.6 – 164.5)	158.3 $\pm$ 6.4 (104.1 – 181.3)	110.3 $\pm$ 7.7 (96.9 – 134.6)

¹ Conductivity in micro-seimens per centimeter ($\mu\text{S}/\text{cm}$); concentrations in micro-equivalents per liter (μeqL^{-1})

² Acid-neutralizing capacity (ANC) was added to this project's analytical suite in 2005

3.1.3 Cosby Creek Water Chemistry

Cosby Creek WQ data were collected at four stream locations: Sites 4, 114, 137 and 492. These sites have been monitored since program inception (1993). Table 14 summarizes the mean $\pm$ standard error (plus range of measured values) for the current year. 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.

Table 14. Summary of Cosby stream water chemistry in 2015. Values shown are mean $\pm$ standard error of the mean (plus range of values in parentheses).

Parameter	Site 4	Site 114	Site 137	Site 492
pH	5.76 $\pm$ 0.04 (5.62 – 5.87)	6.10 $\pm$ 0.05 (5.94 – 6.26)	5.82 $\pm$ 0.04 (5.64 – 5.89)	6.11 $\pm$ 0.04 (5.99 – 6.24)
Conductivity ¹	14.2 $\pm$ 0.2 (13.7 – 14.8)	17.6 $\pm$ 0.2 (16.8 – 18.2)	15.3 $\pm$ 0.3 (14.6 – 16.3)	18.0 $\pm$ 0.2 (17.2 – 18.4)
ANC ²	10.6 $\pm$ 1.4 (5.9 – 14.2)	30.7 $\pm$ 3.6 (21.5 – 44.9)	9.7 $\pm$ 1.0 (7.2 – 13.1)	27.8 $\pm$ 1.9 (21.3 – 34.1)
Chloride	9.0 $\pm$ 0.6 (7.4 – 11.1)	9.4 $\pm$ 0.4 (8.1 – 10.9)	8.7 $\pm$ 0.3 (7.6 – 9.4)	10.3 $\pm$ 1.1 (8.0 – 15.5)
Nitrate	33.7 $\pm$ 1.9 (25.6 – 38.7)	44.7 $\pm$ 1.2 (40.7 – 49.2)	39.7 $\pm$ 1.9 (33.66 – 46.5)	45.1 $\pm$ 0.7 (42.1 – 47.8)
Sulfate	38.4 $\pm$ 1.4 (35.0 – 43.3)	43.7 $\pm$ 1.0 (40.7 – 47.6)	43.2 $\pm$ 1.6 (39.6 – 49.9)	44.6 $\pm$ 1.8 (36.9 – 49.6)
Sodium	29.4 $\pm$ 1.5 (25.6 – 34.6)	36.3 $\pm$ 2.1 (31.7 – 44.5)	29.6 $\pm$ 1.0 (27.4 – 32.9)	35.5 $\pm$ 1.6 (30.3 – 40.3)
Potassium	9.4 $\pm$ 0.5 (7.5 – 10.7)	10.1 $\pm$ 0.2 (9.2 – 10.8)	9.2 $\pm$ 0.4 (8.0 – 10.5)	10.3 $\pm$ 0.6 (9.0 – 12.4)
Magnesium	24.3 $\pm$ 1.6 (19.5 – 29.1)	36.8 $\pm$ 1.4 (32.1 – 42.6)	26.6 $\pm$ 1.4 (21.6 – 31.7)	36.3 $\pm$ 1.1 (31.9 – 39.5)
Calcium	50.0 $\pm$ 1.4 (46.9 – 55.8)	67.0 $\pm$ 2.5 (60.8 – 78.2)	53.1 $\pm$ 1.8 (47.7 – 59.9)	66.0 $\pm$ 1.6 (60.9 – 71.5)
Base Cations	113.1 $\pm$ 3.8 (102.8 – 128.7)	150.2 $\pm$ 5.8 (136.1 – 175.5)	118.5 $\pm$ 4.0 (106.0 – 134.1)	148.1 $\pm$ 3.6 (136.6 – 157.9)

¹ Conductivity in micro-seimens per centimeter ($\mu\text{S}/\text{cm}$); concentrations in micro-equivalents per liter (μeqL^{-1})

² Acid-neutralizing capacity (ANC) was added to this project's analytical suite in 2005

3.1.4 Little River Water Chemistry

Little River WQ data were collected at eight stream sites: Sites 13, 14, 23, 24, 40, 213, 220 and AQ-EPLR-4 (0LR4). Table 15 summarizes the mean $\pm$ standard error (plus range of measured values) for the year 2015.

Table 15. Summary of East Prong Little River stream water chemistry in 2015. Values shown are mean $\pm$ standard error of the mean (plus range of values in parentheses).

Parameter	Site 13	Site 14	Site 23	Site 24	Site 40	Site 213	Site 220	Site 0LR4
pH	6.45 $\pm$ 0.09 (6.14 – 6.72)	6.44 $\pm$ 0.09 (6.17 – 6.71)	6.46 $\pm$ 0.10 (6.15 – 6.80)	6.56 $\pm$ 0.09 (6.29 – 6.83)	6.15 $\pm$ 0.19 (5.40 – 6.51)	6.16 $\pm$ 0.08 (5.92 – 6.42)	5.58 $\pm$ 0.13 (5.24 – 6.02)	6.11 $\pm$ 0.01 (6.06 – 6.14)
Conductivity ¹	17.9 $\pm$ 1.3 (15.2 – 23.5)	16.4 $\pm$ 0.7 (14.5 – 19.1)	16.9 $\pm$ 1.5 (13.7 – 23.7)	22.3 $\pm$ 1.5 (19.7 – 29.0)	18.9 $\pm$ 2.9 (13.2 – 29.5)	13.7 $\pm$ 1.6 (11.1 – 19.9)	17.2 $\pm$ 1.8 (12.3 – 23.4)	15.2 $\pm$ 1.9 (11.5 – 22.0)
ANC ²	105.1 $\pm$ 15.6 (72.2 – 172.8)	97.8 $\pm$ 17.3 (59.6 – 174.0)	105.9 $\pm$ 27.5 (50.0 – 236.3)	136.8 $\pm$ 16.7 (100.2 – 213.0)	46.2 $\pm$ 14.2 (0.2 – 85.8)	27.2 $\pm$ 2.8 (17.6 – 32.8)	3.8 $\pm$ 5.6 (-11.5 – 22.6)	27.3 $\pm$ 5.4 (13.5 – 46.3)
Chloride	11.8 $\pm$ 0.7 (10.2 – 14.0)	11.5 $\pm$ 1.0 (9.3 – 15.3)	11.2 $\pm$ 0.6 (9.3 – 13.3)	11.7 $\pm$ 0.4 (10.8 – 13.1)	36.7 $\pm$ 16.1 (13.5 – 97.0)	23.2 $\pm$ 9.8 (10.7 – 62.1)	17.5 $\pm$ 2.8 (12.5 – 27.8)	29.5 $\pm$ 9.2 (10.1 – 60.2)
Nitrate	5.8 $\pm$ 0.8 (3.7 – 7.9)	6.2 $\pm$ 0.8 (3.0 – 7.8)	7.1 $\pm$ 0.9 (4.21 – 9.8)	4.7 $\pm$ 0.9 (0.6 – 6.7)	18.2 $\pm$ 9.6 (5.61 – 56.6)	12.4 $\pm$ 2.5 (5.5 – 17.7)	36.0 $\pm$ 5.9 (15.7 – 49.5)	12.5 $\pm$ 1.7 (7.3 – 17.3)
Sulfate	35.0 $\pm$ 1.3 (30.2 – 38.7)	33.4 $\pm$ 1.2 (28.5 – 37.8)	30.1 $\pm$ 0.9 (25.7 – 32.6)	41.4 $\pm$ 1.6 (34.7 – 46.4)	32.3 $\pm$ 1.9 (28.1 – 38.1)	26.9 $\pm$ 2.7 (20.9 – 36.3)	45.5 $\pm$ 10.5 (25.7 – 86.3)	29.6 $\pm$ 1.0 (27.5 – 33.1)
Sodium	43.7 $\pm$ 3.3 (36.2 – 58.0)	40.0 $\pm$ 2.3 (34.2 – 49.0)	37.7 $\pm$ 2.7 (32.0 – 48.4)	53.1 $\pm$ 2.9 (47.8 – 64.6)	70.0 $\pm$ 23.6 (28.3 – 153.4)	47.3 $\pm$ 10.9 (32.7 – 90.1)	34.8 $\pm$ 3.4 (29.0 – 47.6)	55.6 $\pm$ 13.0 (30.7 – 102.1)
Potassium	12.9 $\pm$ 1.0 (10.2 – 15.8)	13.4 $\pm$ 1.1 (10.5 – 17.2)	11.1 $\pm$ 0.7 (9.1 – 13.6)	13.1 $\pm$ 0.9 (10.1 – 15.7)	19.0 $\pm$ 4.4 (10.4 – 34.5)	13.1 $\pm$ 1.9 (9.9 – 20.5)	15.8 $\pm$ 1.5 (10.3 – 18.8)	15.5 $\pm$ 2.1 (9.3 – 21.4)
Magnesium	38.5 $\pm$ 5.6 (29.0 – 65.5)	28.7 $\pm$ 2.3 (25.2 – 39.3)	41.3 $\pm$ 8.1 (27.5 – 79.8)	48.9 $\pm$ 5.4 (40.2 – 73.9)	20.7 $\pm$ 0.4 (19.4 – 21.5)	17.0 $\pm$ 0.6 (15.6 – 18.9)	18.8 $\pm$ 0.9 (16.8 – 21.7)	17.6 $\pm$ 0.6 (16.1 – 19.5)
Calcium	73.5 $\pm$ 8.4 (58.4 – 113.6)	63.7 $\pm$ 5.4 (54.6 – 89.0)	65.9 $\pm$ 10.6 (47.9 – 116.1)	96.7 $\pm$ 11.1 (76.7 – 148.5)	47.3 $\pm$ 1.2 (43.8 – 50.1)	31.9 $\pm$ 1.0 (29.1 – 35.2)	47.5 $\pm$ 7.7 (31.6 – 76.4)	33.1 $\pm$ 2.5 (29.7 – 42.9)
Base Cations	168.7 $\pm$ 17.9 (133.9 – 252.6)	145.8 $\pm$ 10.5 (125.1 – 192.2)	156.1 $\pm$ 21.6 (118.9 – 256.5)	211.7 $\pm$ 19.9 (178.2 – 302.3)	157.0 $\pm$ 27.4 (110.5 – 252.5)	109.2 $\pm$ 12.6 (91.3 – 159.3)	117.0 $\pm$ 8.8 (89.9 – 143.2)	121.8 $\pm$ 17.6 (86.3 – 185.8)

¹ Conductivity in micro-seimens per centimeter ($\mu\text{S}/\text{cm}$); concentrations in micro-equivalents per liter (μeqL^{-1})

² Acid-neutralizing capacity (ANC) was added to this project's analytical suite in 2005

3.1.5 Deep Creek Water Chemistry

Deep Creek WQ monitoring data were collected at five stream sites: Sites 255, 256, 259, 326 and INC1.5. Table 16 summarizes the mean $\pm$ standard error (plus range of measured values) for 2015. Sites are presented in upstream to downstream sequence.

Table 16. Summary of Deep Creek stream water chemistry in 2015. Values shown are mean $\pm$ standard error of the mean (plus range of values in parentheses).

Parameter	Site 255	Site 256	Site 259	Site 326	Site INC1.5
pH	6.28 $\pm$ 0.10 (6.09 – 6.40)	6.43 $\pm$ 0.09 (6.26 – 6.57)	6.41 $\pm$ 0.06 (6.29 – 6.52)	6.46 $\pm$ 0.06 (6.40 – 6.58)	6.52 $\pm$ 0.07 (6.40 – 6.64)
Conductivity ¹	14.8 $\pm$ 0.4 (14.1 – 15.6)	13.8 $\pm$ 0.7 (12.5 – 15.0)	12.6 $\pm$ 0.3 (12.1 – 12.9)	14.3 $\pm$ 0.3 (14.0 – 15.0)	12.6 $\pm$ 0.5 (11.6 – 13.3)
ANC ²	32.1 $\pm$ 5.0 (26.8 – 42.1)	49.6 $\pm$ 6.4 (37.0 – 57.2)	42.4 $\pm$ 3.2 (38.3 – 48.6)	67.3 $\pm$ 7.4 (54.7 – 80.2)	63.0 $\pm$ 6.5 (50.3 – 71.8)
Chloride	10.6 $\pm$ 1.0 (9.2 – 12.6)	11.1 $\pm$ 1.6 (8.5 – 14.0)	9.5 $\pm$ 0.8 (8.5 – 11.1)	10.3 $\pm$ 0.7 (9.0 – 11.3)	10.8 $\pm$ 0.8 (9.9 – 12.4)
Nitrate	29.3 $\pm$ 1.0 (28.0 – 31.3)	12.7 $\pm$ 5.0 (2.6 – 17.9)	8.5 $\pm$ 1.7 (5.58 – 11.3)	6.4 $\pm$ 0.7 (5.4 – 7.8)	0.6 $\pm$ 0.5 (0.07 – 1.6)
Sulfate	34.5 $\pm$ 1.1 (33.4 – 36.8)	29.4 $\pm$ 8.5 (19.8 – 46.2)	21.2 $\pm$ 1.1 (19.0 – 22.4)	21.3 $\pm$ 0.9 (19.9 – 23.1)	12.7 $\pm$ 1.5 (11.1 – 15.8)
Sodium	38.6 $\pm$ 3.6 (34.6 – 45.8)	36.6 $\pm$ 3.4 (32.6 – 43.4)	37.5 $\pm$ 2.5 (34.7 – 42.6)	41.1 $\pm$ 3.5 (36.8 – 48.0)	46.2 $\pm$ 3.1 (40.6 – 51.1)
Potassium	7.6 $\pm$ 0.3 (7.1 – 8.1)	9.2 $\pm$ 0.2 (8.8 – 9.4)	10.3 $\pm$ 0.7 (9.1 – 11.4)	12.2 $\pm$ 0.3 (11.7 – 12.6)	14.1 $\pm$ 0.8 (12.8 – 15.7)
Magnesium	25.3 $\pm$ 0.8 (23.7 – 26.5)	20.8 $\pm$ 0.2 (20.5 – 21.3)	20.4 $\pm$ 0.4 (20.0 – 21.2)	24.0 $\pm$ 1.8 (20.8 – 27.2)	18.7 $\pm$ 1.1 (16.5 – 20.0)
Calcium	51.2 $\pm$ 1.5 (48.9 – 54.1)	44.1 $\pm$ 1.3 (41.8 – 46.4)	38.3 $\pm$ 1.5 (35.4 – 40.3)	43.6 $\pm$ 2.8 (38.8 – 48.6)	32.7 $\pm$ 2.4 (27.9 – 35.2)
Base Cations	122.7 $\pm$ 5.5 (115.5 – 133.5)	110.7 $\pm$ 4.7 (104.3 – 119.9)	106.5 $\pm$ 3.4 (102.2 – 113.1)	120.8 $\pm$ 8.2 (108.1 – 136.0)	111.8 $\pm$ 6.5 (98.8 – 118.7)

¹ Conductivity in micro-seimens per centimeter ($\mu\text{S}/\text{cm}$); concentrations in micro-equivalents per liter (μeqL^{-1})

² Acid-neutralizing capacity (ANC) was added to this project's analytical suite in 2005

3.1.6 Middle Prong of the Little Pigeon River Water Chemistry

Middle Prong Little Pigeon River WQ data were collected at five stream sites: Sites 47, 48, 52, 371, and MPLP_3. Table 17 summarizes the mean $\pm$ standard error (plus range of measured values) for year 2015.

Table 17. Summary of Middle Prong Little Pigeon River stream water chemistry in 2015. Values shown are mean $\pm$ standard error of the mean (plus range of values in parentheses).

Parameter	Site 47	Site 48	Site 52	Site 371	Site MPLP-3
pH	5.86 $\pm$ 0.06 (5.78 – 5.98)	6.07 $\pm$ 0.07 (6.00 – 6.22)	6.16 $\pm$ 0.17 (5.88 – 6.48)	5.94 $\pm$ 0.24 (5.48 – 6.30)	5.46 $\pm$ 0.06 (5.38 – 5.57)
Conductivity ¹	12.7 $\pm$ 1.0 (11.5 – 14.8)	15.5 $\pm$ 0.4 (14.9 – 16.3)	15.0 $\pm$ 1.9 (11.6 – 18.2)	21.0 $\pm$ 1.5 (19.5 – 24.0)	20.6 $\pm$ 1.4 (18.9 – 23.4)
ANC ²	9.2 $\pm$ 2.1 (6.7 – 13.3)	18.8 $\pm$ 5.2 (13.6 – 29.3)	32.7 $\pm$ 16.7 (7.8 – 64.4)	15.3 $\pm$ 11.7 (-4.4 – 36.0)	-2.5 $\pm$ 1.9 (-4.6 – 1.3)
Chloride	8.7 $\pm$ 0.8 (7.3 – 10.0)	10.2 $\pm$ 0.6 (9.3 – 11.2)	10.5 $\pm$ 1.8 (8.5 – 14.1)	17.8 $\pm$ 6.0 (11.4 – 29.8)	16.3 $\pm$ 5.0 (10.9 – 26.2)
Nitrate	24.8 $\pm$ 3.0 (20.0 – 30.2)	25.8 $\pm$ 2.3 (21.5 – 29.2)	19.5 $\pm$ 2.8 (14.48 – 24.2)	47.5 $\pm$ 3.2 (43.3 – 53.7)	49.7 $\pm$ 3.9 (41.84 – 54.4)
Sulfate	41.3 $\pm$ 7.8 (32.8 – 57.0)	54.2 $\pm$ 5.4 (47.8 – 64.8)	41.5 $\pm$ 1.9 (37.7 – 44.0)	75.5 $\pm$ 8.1 (63.7 – 90.9)	81.8 $\pm$ 10.3 (68.7 – 102.2)
Sodium	25.0 $\pm$ 1.4 (22.6 – 27.5)	31.7 $\pm$ 2.2 (28.6 – 36.0)	34.1 $\pm$ 7.4 (22.0 – 47.5)	39.4 $\pm$ 10.5 (24.6 – 59.7)	33.5 $\pm$ 7.1 (25.3 – 47.6)
Potassium	8.0 $\pm$ 0.7 (7.0 – 9.3)	7.7 $\pm$ 0.5 (6.8 – 8.3)	9.8 $\pm$ 0.3 (9.5 – 10.3)	5.6 $\pm$ 1.7 (3.6 – 9.1)	4.6 $\pm$ 0.7 (3.8 – 6.0)
Magnesium	23.7 $\pm$ 5.9 (17.6 – 35.4)	32.2 $\pm$ 2.6 (29.4 – 37.4)	26.2 $\pm$ 3.6 (20.6 – 32.8)	51.4 $\pm$ 4.0 (45.7 – 59.2)	51.8 $\pm$ 4.2 (45.5 – 59.7)
Calcium	39.0 $\pm$ 4.6 (33.7 – 48.2)	53.0 $\pm$ 1.4 (50.3 – 54.8)	57.1 $\pm$ 12.9 (35.0 – 79.7)	73.0 $\pm$ 6.2 (62.5 – 84.0)	62.1 $\pm$ 3.3 (58.8 – 68.6)
Base Cations	95.7 $\pm$ 9.9 (84.5 – 115.4)	124.5 $\pm$ 5.2 (116.2 – 134.0)	127.1 $\pm$ 24.1 (87.1 – 170.3)	169.5 $\pm$ 21.8 (140.0 – 211.9)	152.0 $\pm$ 15.0 (135.7 – 181.9)

¹ Conductivity in micro-seimens per centimeter ($\mu\text{S}/\text{cm}$); concentrations in micro-equivalents per liter (μeqL^{-1})

² Acid-neutralizing capacity (ANC) was added to this project's analytical suite in 2005

3.1.7 Hazel Creek Water Chemistry

Hazel Creek WQ data were collected at 10 stream sites: Sites 221, 222, 224, 310, 311, 479, 480, 483, 484 and 485. For formatting reasons, the Hazel Creek data are summarized in two tables, one set of five sites are summarized in Table 18 and the other set of five sites in Table 19. Values shown are the mean $\pm$ standard error (plus range of measured values) for year 2015.

Table 18. Summary of Hazel Creek stream water chemistry in 2015. Values shown are mean $\pm$ standard error of the mean (plus range of values in parentheses) for sampling sites 221, 222, 224, 310, and 311.

Parameter	Site 221	Site 222	Site 224	Site 310	Site 311
pH	6.09 $\pm$ 0.05 (6.03 – 6.14)	6.18 $\pm$ 0.01 (6.17 – 6.19)	6.25 $\pm$ 0.05 (6.23 – 6.27)	6.41 $\pm$ 0.12 (6.38 – 6.44)	6.38 $\pm$ 0.05 (6.34 – 6.42)
Conductivity ¹	9.7 $\pm$ 0.9 (8.8 – 10.6)	10.5 $\pm$ 0.5 (10.0 – 11.0)	10.9 $\pm$ 0.2 (10.5 – 11.3)	13.5 $\pm$ 2.8 (12.5 – 14.5)	12.4 $\pm$ 1.2 (11.6 – 13.2)
ANC ²	27.8 $\pm$ 6.0 (21.9 – 33.8)	28.1 $\pm$ 1.5 (26.6 – 29.6)	43.7 $\pm$ 1.6 (42.9 – 44.6)	70.0 $\pm$ 18.6 (69.4 – 70.7)	58.2 $\pm$ 8.7 (55.7 – 60.7)
Chloride	9.2 $\pm$ 0.1 (9.1 – 9.4)	9.7 $\pm$ 0.2 (9.5 – 10.0)	10.0 $\pm$ 0.9 (9.9 – 10.1)	10.9 $\pm$ 1.0 (10.8 – 11.0)	11.0 $\pm$ 0.6 (10.9 – 11.0)
Nitrate	17.0 $\pm$ 2.9 (14.0 – 19.9)	17.7 $\pm$ 0.2 (17.5 – 18.0)	10.1 $\pm$ 0.3 (8.74 – 11.4)	4.6 $\pm$ 2.0 (4.1 – 5.1)	4.9 $\pm$ 1.6 (4.41 – 5.3)
Sulfate	13.2 $\pm$ 5.0 (8.2 – 18.2)	14.7 $\pm$ 1.7 (13.0 – 16.3)	14.4 $\pm$ 0.6 (13.0 – 15.8)	18.3 $\pm$ 7.0 (18.0 – 18.7)	15.9 $\pm$ 3.3 (15.3 – 16.5)
Sodium	36.7 $\pm$ 9.7 (27.0 – 46.3)	33.7 $\pm$ 4.3 (29.5 – 38.0)	37.0 $\pm$ 1.8 (34.9 – 39.2)	44.1 $\pm$ 7.7 (39.0 – 49.2)	41.0 $\pm$ 4.1 (36.4 – 45.5)
Potassium	8.2 $\pm$ 0.3 (7.9 – 8.6)	8.5 $\pm$ 0.1 (8.5 – 8.6)	9.2 $\pm$ 1.2 (9.1 – 9.2)	10.3 $\pm$ 2.1 (9.7 – 10.9)	10.5 $\pm$ 1.0 (10.5 – 10.6)
Magnesium	15.9 $\pm$ 1.4 (14.5 – 17.2)	16.7 $\pm$ 1.5 (15.2 – 18.2)	16.8 $\pm$ 1.5 (15.7 – 17.9)	25.5 $\pm$ 12.0 (22.6 – 28.4)	21.7 $\pm$ 4.9 (19.6 – 23.8)
Calcium	25.7 $\pm$ 1.7 (24.0 – 27.5)	28.8 $\pm$ 3.0 (25.8 – 31.7)	31.7 $\pm$ 3.1 (29.7 – 33.8)	45.3 $\pm$ 12.8 (39.9 – 50.8)	38.4 $\pm$ 5.1 (34.6 – 42.3)
Base Cations	86.5 $\pm$ 12.5 (74 – 99)	87.8 $\pm$ 8.7 (79.1 – 96.4)	94.7 $\pm$ 5.1 (89.5 – 100.0)	125.2 $\pm$ 34.6 (111.2 – 139.2)	111.6 $\pm$ 14.3 (101.0 – 122.3)

¹ Conductivity in micro-seimens per centimeter ($\mu\text{S}/\text{cm}$); concentrations in micro-equivalents per liter (μeqL^{-1})

² Acid-neutralizing capacity (ANC) was added to this project's analytical suite in 2005

Table 19. Summary of Hazel Creek stream water chemistry in 2015. Values shown are the mean $\pm$ standard error of the mean (plus range of values in parentheses) for sampling sites 479, 480, 483, 484, and 485.

Parameter	Site 479	Site 480	Site 483	Site 484	Site 485
pH	6.38 $\pm$ 0.07 (6.32 - 6.45)	6.42 $\pm$ 0.03 (6.40 - 6.45)	6.34 $\pm$ 0.06 (6.28 - 6.39)	6.35 $\pm$ 0.12 (6.23 - 6.46)	6.36 $\pm$ 0.05 (6.31 - 6.41)
Conductivity ¹	13.2 $\pm$ 1.3 (12.8 - 13.6)	14.6 $\pm$ 1.2 (13.4 - 15.7)	13.4 $\pm$ 1.2 (12.2 - 14.6)	13.7 $\pm$ 1.8 (10.9 - 16.5)	12.5 $\pm$ 1.0 (11.5 - 13.5)
ANC ²	70.6 $\pm$ 9.0 (63.9 - 77.2)	79.8 $\pm$ 0.4 (79.4 - 80.2)	62.6 $\pm$ 11.2 (51.4 - 73.8)	72.1 $\pm$ 11.4 (53.5 - 90.7)	62.7 $\pm$ 0.9 (61.7 - 63.6)
Chloride	12.4 $\pm$ 0.6 (12.1 - 12.7)	11.3 $\pm$ 0.5 (10.8 - 11.8)	11.5 $\pm$ 0.1 (11.3 - 11.6)	11.4 $\pm$ 0.7 (10.4 - 12.5)	10.4 $\pm$ 0.2 (10.2 - 10.6)
Nitrate	4.3 $\pm$ 1.7 (3.6 - 5.0)	1.9 $\pm$ 0.9 (1.0 - 2.9)	5.8 $\pm$ 2.9 (2.8 - 8.7)	3.7 $\pm$ 1.8 (1.74 - 5.7)	4.7 $\pm$ 2.2 (2.5 - 6.9)
Sulfate	15.5 $\pm$ 3.5 (15.3 - 15.7)	19.4 $\pm$ 0.2 (19.2 - 19.6)	21.1 $\pm$ 5.5 (15.6 - 26.6)	20.5 $\pm$ 4.7 (13.5 - 27.4)	16.4 $\pm$ 2.9 (13.5 - 19.4)
Sodium	45.5 $\pm$ 4.2 (42.0 - 48.9)	48.1 $\pm$ 5.3 (42.8 - 53.4)	42.4 $\pm$ 0.8 (41.5 - 43.2)	43.2 $\pm$ 5.4 (35.4 - 50.9)	40.1 $\pm$ 4.6 (35.5 - 44.7)
Potassium	12.1 $\pm$ 1.0 (11.3 - 13.0)	12.7 $\pm$ 0.7 (11.9 - 13.4)	11.3 $\pm$ 1.2 (10.2 - 12.5)	12.3 $\pm$ 1.4 (10.2 - 14.5)	10.9 $\pm$ 0.4 (10.6 - 11.3)
Magnesium	22.5 $\pm$ 5.2 (20.9 - 24.2)	29.9 $\pm$ 3.2 (26.6 - 33.1)	26.2 $\pm$ 5.7 (20.5 - 31.8)	28.5 $\pm$ 7.6 (16.5 - 40.4)	21.9 $\pm$ 2.9 (18.9 - 24.8)
Calcium	39.9 $\pm$ 5.4 (36.1 - 43.6)	45.2 $\pm$ 5.1 (40.1 - 50.3)	39.9 $\pm$ 1.9 (38.0 - 41.7)	42.5 $\pm$ 8.2 (29.8 - 55.3)	38.9 $\pm$ 5.7 (33.2 - 44.7)
Base Cations	120.0 $\pm$ 15.0 (112.0 - 128.0)	135.8 $\pm$ 14.4 (121.4 - 150.2)	119.7 $\pm$ 7.9 (111.9 - 127.6)	126.5 $\pm$ 22.3 (91.9 - 161.1)	111.8 $\pm$ 13.6 (98.2 - 125.5)

¹ Conductivity in micro-seimens per centimeter ($\mu\text{S}/\text{cm}$); concentrations in micro-equivalents per liter (μeqL^{-1})

² Acid-neutralizing capacity (ANC) was added to this project's analytical suite in 2005

3.2 Vital Signs Water Chemistry: Toxicological Thresholds

Schwartz et al. (2014) reviewed the aquatic toxicology literature for threshold levels of pH, aluminum, and zinc. These water quality parameters are pertinent to aquatic biological function; aquatic biota is at greater risk of adverse biological effects when exposed to water with these parameters outside of tolerable (or necessary) levels. For example, growth of trout species is documented to be inhibited when water pH < 5.5, and trout abundance is reduced when water pH < 5.0. Similarly, concentrations of metals (such as aluminum and zinc) above species-specific effects thresholds can adversely affect the normal function of some aquatic biota. Table 20 summarizes the comparison of water quality results for 2015 Park-wide stream samples to the documented threshold effects levels. The table summarizes the instances (counts) when water samples contained the corresponding parameter at the indicated level or concentration.

Table 20. Number of instances during year 2015 in which water samples showed water chemistry outside of established thresholds. Water chemistry parameters summarized are: pH, acid-neutralization capacity (ANC), total dissolved aluminum (Al) and zinc (Zn), and base cation surplus (BCS). Values indicate number of instances of threshold non-compliance, not the number of sites in the watershed.

Watershed	pH < 6.0	ANC < 20 (µeq/L)	Al > 0.08 (mg/L)	Zn > 0.047 (mg/L)	BCS < 0 (µeq/L)*	Total Count
Cosby Creek	14	12	3	0	0	29
Pigeon River (Middle Prong)	9	11	0	0	2	22
Little River (East Prong)	6	7	2	0	0	15
Abrams Creek (Anthony Creek tributary)	4	4	0	0	0	8
Cataloochee Creek	2	1	1	0	1	5
Abrams Creek (main stem)	0	0	0	0	0	0
Abrams Creek (Mill Creek tributary)	0	0	0	0	0	0
Deep Creek	0	0	0	0	0	0
Hazel Creek	0	0	0	0	0	0
Total Count	35	35	6	0	3	76

* BCS = base cation surplus = sum(Na, K, Mg, Ca) – sum(Cl, NO₃, SO₄)

3.2.1 pH

Reported in Table 20 are the cumulative numbers of instances when water quality of stream samples did not meet a designated threshold value. Of the 207 Park-wide stream water samples collected in 2015, 35 samples had pH < 6.0, and 35 samples had ANC < 20 µeq L⁻¹. The correspondence in number for pH and ANC is a good check on internal consistence and data quality, because pH and ANC are related water quality parameters. These instances of non-compliance were associated with 16 of the 49 monitored sites scattered throughout five of the seven monitored watersheds, with no apparent correlation to location or elevation. The lowest measured pH and ANC in 2015 was 5.24 and -11.5 µeq L⁻¹, respectively, and was associated with the September sample from Site 220 (East Prong Little River). The distribution of pH and ANC levels throughout the GRSM as measured at

the current monitoring sites is depicted in Figure 10. Locations with pH and ANC above or below threshold criteria are shown as yellow circles and red squares, respectively.

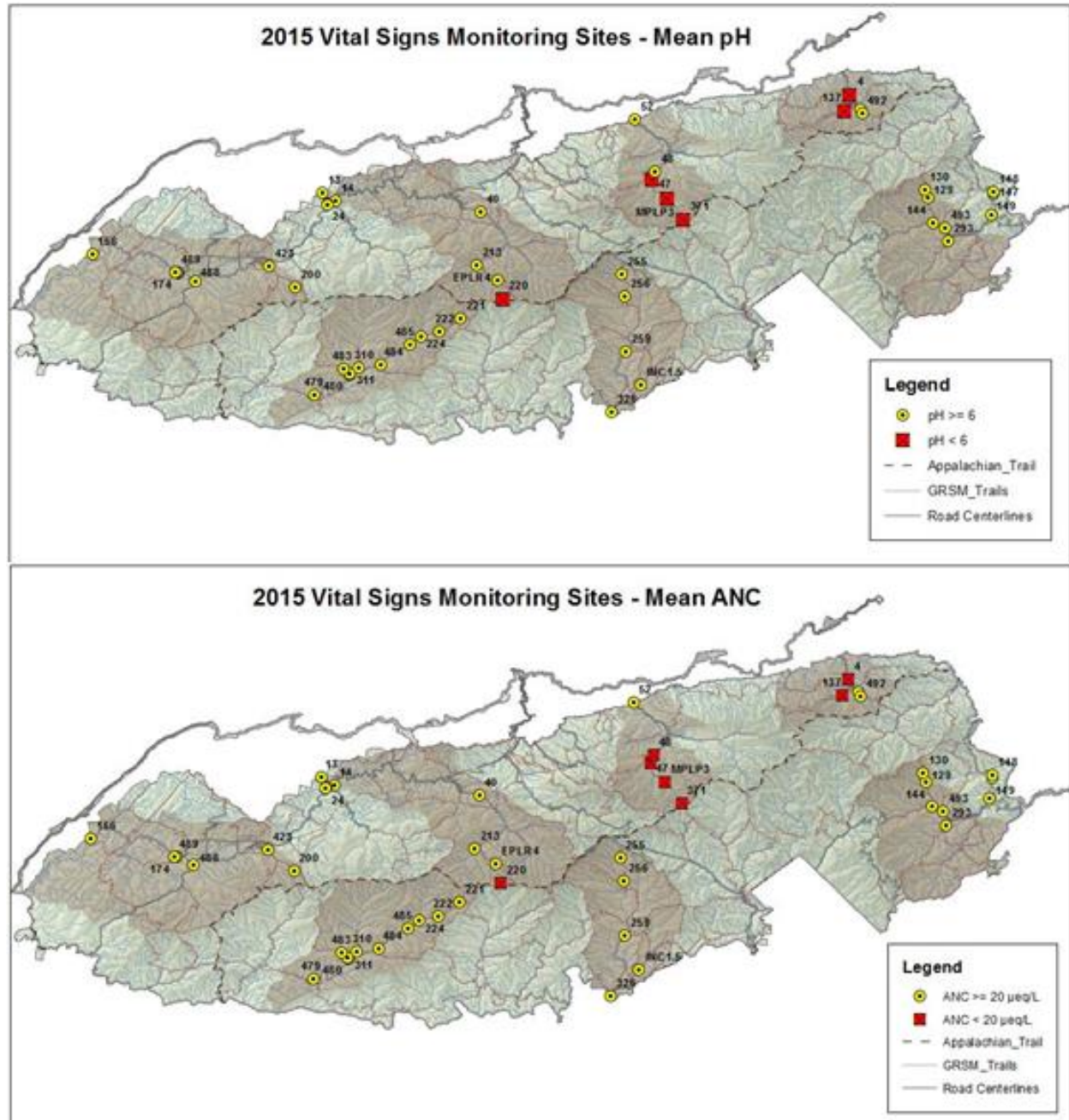


Figure 10. Distribution of pH and acid-neutralizing capacity (ANC) at current Vital Signs water quality monitoring sites in 2015. Yellow circles indicate pH > 6.0 and ANC > 20 micro-equivalents per liter; red squares indicate measured values below those criteria.

3.2.2 Aluminum

The selected threshold value for total dissolved aluminum (Al) is 0.08 mg/L (Schwartz et al. 2014). This may be a toxicologically relevant concentration threshold; however, concentrations that induce toxicity may differ widely for different organisms, and may be strongly dependent on speciation and complexation with dissolved ligands such as large organic compounds (Burns 1989). In 2015, only four samples had a total dissolved aluminum concentration above the criterion value. One site was from the Little River watershed (Site 220 with two instances), one was from the Cataloochee watershed (Site 130 with one instance), and two were from the Cosby watershed (Sites 4 with one instance, and Site 114 with two instances). Unsurprisingly, highest aluminum concentration measured in 2015 ([Al] = 0.22 mg/L) was associated with the stream sample with the lowest pH (5.24) and lowest ANC ($-11.5 \mu\text{eq L}^{-1}$): Double Springs Gap Shelter Site 220 in the Little River watershed.

3.2.3 Zinc

The selected threshold value for total dissolved zinc (Zn) was 0.047 mg/L (Schwartz et al. 2014). None of the stream survey sites had zinc concentrations above this value in 2015.

3.2.4 Base Cation Surplus

An indicator of ion chemistry balance in the watersheds is the difference between total equivalents of “base cations” (non-hydrolyzing positively charged metals: sodium, potassium, magnesium and calcium) and the measured anions (chloride, nitrate and sulfate). This is termed the base cation surplus (BCS). Under conditions of stress in the watershed system, excessive loss of ANC occurs as loss of exchangeable ions. In 2015, there were only three instances in which BCS was less than zero, one of which was an aberrant result from Site 129 (Cataloochee watershed) suspected to be an outlier due to some unknown analytical error or sample corruption (i.e., uncharacteristically high chloride concentration by a factor of 10 over other samples, or previous years’ results from the same site). The other two instances of BCS below zero were from samples in the Little Pigeon River watershed: Sites 371 and AQ_MPLP_3. Both were only marginally below zero, and very well could be within experimental error of zero (perfect balance).

3.3 Vital Signs Water Chemistry: Elevation Gradients

Primary water quality parameters (pH, ANC, sulfate and nitrate concentrations) are qualitative indicators of biogeochemical processes occurring within the drainage area. Annual mean values for these parameters were calculated for each site sampled throughout 2015. Those mean values were plotted against elevation (feet above mean sea level) to illustrate potential relationships between stream water quality and elevation. Figure 11 is a four-panel illustration showing plots of sample site elevation against pH, ANC ($\mu\text{eq L}^{-1}$), sulfate ($\mu\text{eq L}^{-1}$), and nitrogen ($\mu\text{eq L}^{-1}$), respectively.

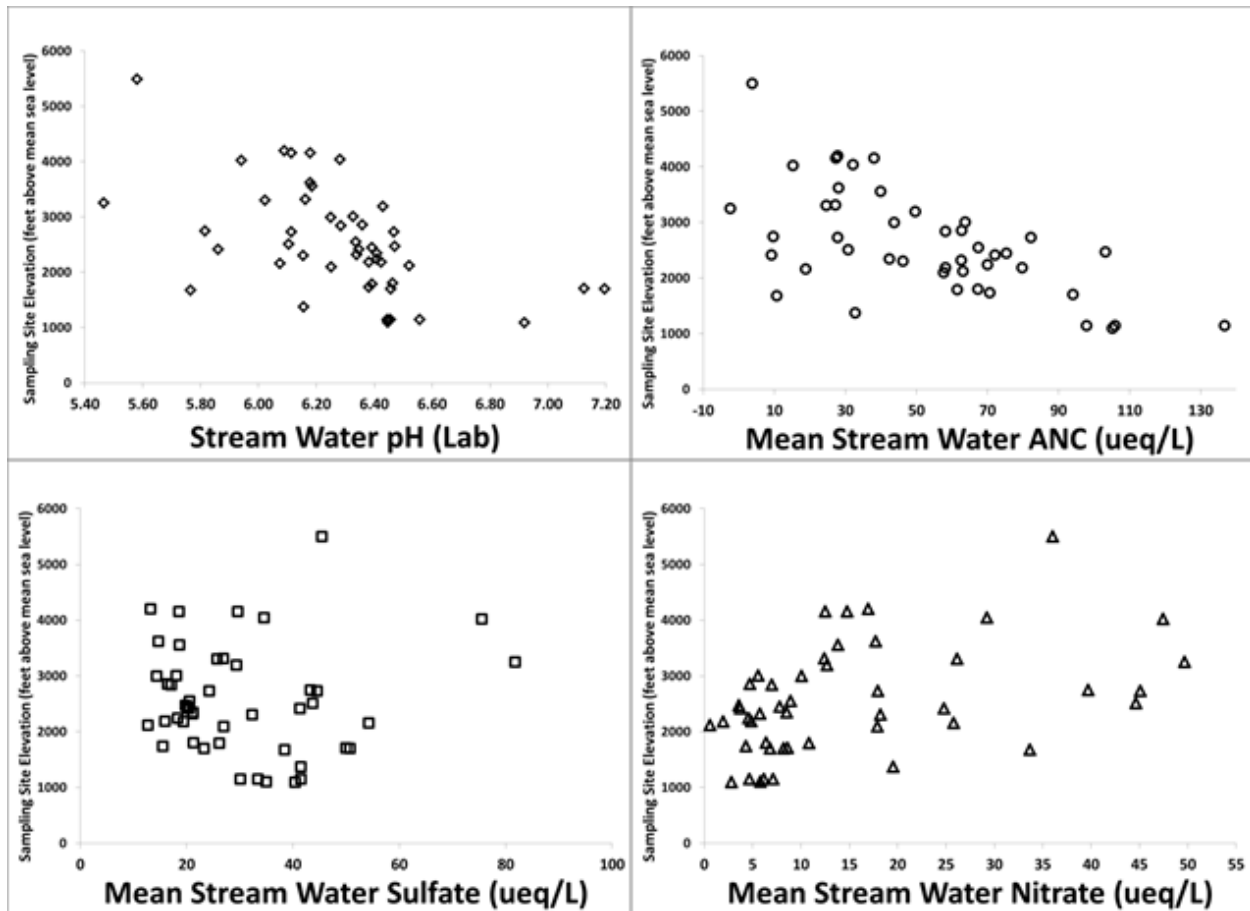


Figure 11. Illustrations of water quality parameters as a function of site elevation (MSL feet) in 2015. Parameters plotted are: pH (upper left), ANC (upper right), sulfate (lower left), and nitrate (lower right).

4.0 Laboratory Data Quality Evaluations

Data quality was assessed by analyzing various prepared water samples of known composition (blanks, duplicates and fortified “spike” samples) and a set of performance evaluation samples of known composition supplied by an independent source (U.S. Geological Survey [USGS] inter-laboratory comparison study standard reference samples; <https://bqs.usgs.gov/srs>), collectively known as quality assurance (QA) samples. The analytical results of these QA samples’ are summarized using the following data quality parameters:

- Analyte detection limits (DL) of unprocessed laboratory deionized water (instrument detection limits; IDL)
- Analyte DL of laboratory deionized water processed in the laboratory (Method Blanks) by the same method as regular field samples (method detection limits; MDL)
- Analyte concentrations in laboratory-processed Method Blanks
- Analyte concentrations in Trip Blanks (portions of laboratory deionized water taken into the field during sampling events, exposed to environmental conditions, and returned to the laboratory with collected field samples)
- Precision (percentage) of laboratory split samples (two separate portions of the same field sample, processed in the laboratory identically and in parallel)
- Precision (percentage) of field duplicate samples (two separate field samples collected concurrently from the same sampling location in the field)
- Accuracy (percentage) of recovery of known analyte amounts spiked into field samples (matrix spiked field sample)
- Accuracy (percentage) of analyte concentrations measured in laboratory-prepared continuing calibration verification (CCV) samples (prepared to match the low-concentration calibration standard solution)
- Accuracy (percentage) of analyte concentrations measured in independent-sourced (USGS) performance evaluation samples

Current year’s Vital Signs monitoring data quality is reported for autotitrator data (pH, conductivity and ANC), ion chromatography (IC) data (anions and cations), and inductively-coupled argon plasma atomic emission spectrometry (iCAP) data (dissolved metals).

In 2015, a total of 481 stream water samples were analyzed, allocated as follows.

- 216 samples from NDW: OS/TF precipitation, soil lysimeters, and SW/NE streamlets
- 207 Park-wide “Vital Signs” stream samples, plus 31 trip blanks and 27 field duplicate

4.1 Data Quality: Laboratory Quality Assurance Samples

Table 21 presents the data quality assessment of laboratory QA samples prepared in 2015. For each parameter, calculated statistics shown are the mean $\pm$ the standard error of the mean. The mean concentrations of measured parameters in method blanks and field sample blanks generally were between the IDL and MDL. The acceptance criterion for precision is $\pm 20\%$; all duplicate precision results for 2015 were within the acceptable tolerance range. The acceptance criterion for QA accuracy of matrix spike and or performance evaluation samples is 80%-120%; all QA accuracy results for 2015 were within the acceptable tolerance range.

4.2 Data Quality: Independent Performance Evaluation Samples

Certified quality assurance standard reference samples (SRS) were obtained from the USGS as part of an inter-laboratory quality assessment study. The current year SRS and the two most recent archived SRS samples were analyzed periodically throughout the year. Overall mean measured concentrations were compared to the published Most Probable Values (MPV) in the SRS (found at <http://bqs.usgs.gov/srs/>). USGS QA samples analyzed this year were:

- T-223, N-127 and P-65 (Fall 2015 round)
- T-219, N-123 and P-63 (Fall 2014 round)
- T-217, N-121 and P-62 (Spring 2014 round)

Tables 22a, 22b, and 22c summarize the measured accuracy (as percentage of MPV) for dissolved anions and cations measured by IC, and dissolved metals measured by iCAP.

Table 21. Summary of 2015 data quality assessment on laboratory QA samples. Detection limits and sample blanks are shown as concentrations in mg/L (except for pH, conductivity and ANC).

Parameter	Detection Limits (DL) ¹		Sample Blanks ²		Duplicate Precision (%) ²		Bias/Recovery (%) ²	
	Instrument	Method	Method (Lab)	Trip (Field)	Lab Split	Field	Matrix Spike	Lab CCV
pH	n.a.	n.a.	5.71 ± 0.01	5.73 ± 0.04	n.a.	0.94 ± 0.26%	n.a.	n.a.
Conductivity ³	n.a.	n.a.	2.54 ± 0.06	2.19 ± 0.07	n.a.	6.94 ± 3.43%	n.a.	n.a.
ANC ⁴	n.a.	n.a.	0.96 ± 0.19	0.45 ± 0.34	n.a.	14.29 ± 2.81%	n.a.	n.a.
Chloride ⁵	0.020	0.061	0.033 ± 0.006	0.020 ± 0.004	1.06 ± 0.67%	9.68 ± 2.97%	102.7 ± 0.3%	n.a.
Nitrate	0.023	0.085	0.045 ± 0.009	0.040 ± 0.003	1.98 ± 1.07%	5.08 ± 1.38%	102.7 ± 0.4%	n.a.
Sulfate	0.010	0.004	< IDL and < MDL	< IDL and < MDL	0.59 ± 0.76%	3.52 ± 2.07%	101.7 ± 0.2%	n.a.
Ammonium	0.0021	0.0027	0.0029 ± 0.0002	< IDL and < MDL	2.33 ± 1.58%	< IDL	99.1 ± 1.5%	n.a.
Sodium	0.034	0.081	0.034 ± 0.007	< IDL and < MDL	0.47 ± 0.64%	5.57 ± 1.44%	102.4 ± 0.9%	99.1 ± 0.6%
Potassium	0.001	0.008	0.005 ± 0.001	0.009 ± 0.001	0.27 ± 0.88%	7.76 ± 2.93%	102.1 ± 0.7%	97.3 ± 0.5%
Magnesium	0.001	0.006	0.003 ± 0.001	0.006 ± 0.0005	-0.45 ± 0.31%	1.57 ± 0.45%	101.5 ± 0.5%	101.1 ± 0.3%
Calcium	0.007	0.029	0.014 ± 0.003	0.033 ± 0.003	0.40 ± 0.68%	1.88 ± 0.45%	98.4 ± 1.1%	99.4 ± 0.3%
Aluminum	0.0011	0.0600	0.0162 ± 0.0053	0.0072 ± 0.0014	0.20 ± 1.16%	< IDL	100.2 ± 0.6%	101.1 ± 0.3%
Copper	0.0005	0.0009	< IDL and < MDL	0.0008 ± 0.0003	< IDL	< IDL	101.8 ± 0.6%	101.5 ± 0.4%
Iron	0.0006	0.0206	0.0055 ± 0.0018	0.0037 ± 0.0005	< IDL	< IDL	100.7 ± 0.3%	98.0 ± 0.2%
Manganese	0.0004	0.0003	< IDL	0.0007 ± 0.0002	< IDL	< IDL	101.5 ± 0.3%	101.0 ± 0.3%
Silica	0.022	0.047	0.025 ± 0.004	< IDL and < MDL	-0.32 ± 0.27%	1.40 ± 0.53%	99.5 ± 0.5%	103.4 ± 0.3%
Zinc	0.0006	0.0026	< IDL	0.0009 ± 0.0002	< IDL	< IDL	100.1 ± 0.5%	97.9 ± 0.3%

¹ Detection limits for pH and acid-neutralizing capacity (ANC) are not applicable to this report. Both parameters are related to the sample hydrogen ion concentration which can not reach zero values in water samples under typical environmental conditions.

² Precision value after the ± symbol is the standard error of the mean (calculated as: standard deviation ÷ square-root of number of data points)

³ Conductivity in micro-seimens per centimeter (µS/cm)

⁴ Acid-neutralizing capacity (ANC) results are shown in micro-equivalents per liter (µeq L⁻¹)

⁵ Analyte concentrations (detection limits and sample blanks) are shown in milligrams per liter (mg L⁻¹)

Table 22a. Summary of 2015 accuracy results for performance evaluation samples from the U.S. Geological Survey: Low-concentration nutrient water sample. Values shown are mean $\pm$ standard error; single values are for unstable samples.

Parameter	N-127	N-123	N-121
ammonium (as N)	105.2%	102.1%	110.9%
nitrate (as N)	100.1%	94.8%	83.8%

¹ Independent performance evaluation samples consist of Fall 2015, Fall 2014 and Spring 2014 standard reference samples (SRS) obtained from the U.S. Geological Survey (USGS). UTK-CEE is designated as "lab #228" (<http://bqs.usgs.gov/srs/>).

Table 22b. Summary of 2015 accuracy results for performance evaluation samples from the U.S. Geological Survey: Precipitation water sample. Values shown are mean $\pm$ standard error; single values are for unstable samples.

Parameter	P-65	P-63	P-62
pH	100.1%	100.5%	92.1%
conductivity	104.7%	98.2%	100.0%
chloride	107.1%	104.1%	110.8%
sulfate	93.4%	85.2%	104.7%

¹ Independent performance evaluation samples consist of Fall 2015, Fall 2014 and Spring 2014 standard reference samples (SRS) obtained from the U.S. Geological Survey (USGS). UTK-CEE is designated as "lab #228" (<http://bqs.usgs.gov/srs/>).

Table 22c. Summary of 2015 accuracy results for performance evaluation samples from the U.S. Geological Survey: Trace metal water sample. Values shown are mean $\pm$ standard error; single values are for unstable samples.

Parameter	T-223	T-219	T-217
sodium	101.9 $\pm$ 0.5%	102.8 $\pm$ 0.7%	102.2 $\pm$ 0.7%
potassium	115.4 $\pm$ 0.7%	123.8 $\pm$ 0.8%	120.6 $\pm$ 0.6%
magnesium	100.0 $\pm$ 0.5%	98.2 $\pm$ 0.5%	98.6 $\pm$ 1.5%
calcium	102.2 $\pm$ 0.4%	100.4 $\pm$ 0.5%	99.6 $\pm$ 0.5%
aluminum	102.0 $\pm$ 0.4%	96.3 $\pm$ 0.5%	100.7 $\pm$ 0.7%
copper	106.1 $\pm$ 1.7%	104.7 $\pm$ 0.6%	102.4 $\pm$ 1.5%
iron	100.7 $\pm$ 0.4%	99.4 $\pm$ 0.5%	99.6 $\pm$ 0.7%
manganese	101.6 $\pm$ 0.5%	99.7 $\pm$ 0.5%	98.1 $\pm$ 0.6%
silica	100.5 $\pm$ 0.3%	100.8 $\pm$ 0.5%	100.2 $\pm$ 0.5%
zinc	102.0 $\pm$ 0.9%	102.9 $\pm$ 0.6%	100.4 $\pm$ 0.5%

¹ Independent performance evaluation samples consist of Fall 2015, Fall 2014 and Spring 2014 standard reference samples (SRS) obtained from the U.S. Geological Survey (USGS). UTK-CEE is designated as "lab #228" (<http://bqs.usgs.gov/srs/>).

4.3 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 ($\mu\text{eq/L}$) 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 2015 NDW samples are summarized in Table 23. 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. The charge balance deviation in OS samples is likely due to high relative error inherent in low-concentration analyses.

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. On average, all other sample types had positive charge balance deviations, which indicate 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 carbonate 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.

Table 23. Summary of 2015 ion charge balance (as mean percent difference $\pm$ 1 standard deviation) of Noland Divide water samples (streamlets, precipitation and soil water). Large variation reflects systematic seasonal changes in ion composition of samples.

Watershed Sample Type	NE Streamlet	SW Streamlet	TF* (buckets)	TF* (funnels)	OS OpenSite	Soil Water (A-horizon)	Soil Water (Bw-horizon)	Soil Water (Cb-horizon)
Annual Mean $\pm$ 1 Std.Dev	14.5 $\pm$ 7.5%	14 $\pm$ 7.6%	25.6 $\pm$ 17.7%	43.1 $\pm$ 17.5%	17.7 $\pm$ 17.3%	-2.9 $\pm$ 10.1%	-6.9 $\pm$ 14.4%	-3.2 $\pm$ 16.4%
No. of samples	N = 26	N = 26	N = 17	N = 15	N = 22	N = 45	N = 22	N = 31

* 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: Analytical Methods Used by 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

¹ Standard Methods, 1999. Standard Methods for the Examination of Water and Wastewater, 20th Edition. Editors: Lenore S. Clesceri, Arnold E. Greenberg and Andrew D. Eaton. American Public Health Association (APHA), American Water Works Association (AWWA), and the Water Environment Federation (WEF). United Book Press, Inc.; Baltimore, MD.

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

Station ID	Station Name	Latitude	Longitude	Elevation (meters)	Stream Order	Stream System
GRSM_F_0200	Anthony Creek Above Campsite 9	35.577800	-83.740770	1013.8	2	ABC-Anthony
GRSM_F_0423	Anthony Creek above horse camp where road crosses stream	35.59798	-83.7659	638.9	3	ABC-Anthony
GRSM_F_0173	Mill Creek Above Abrams Creek	35.590886	-83.853059	518.5	4	ABC-Mill
GRSM_F_0488	Mill Creek at Pumphouse on Forge Creek Road	35.583519	-83.836685	545.7	3	ABC-Mill
GRSM_F_0156	Abrams Creek at Ranger Station	35.609044	-83.934932	334.2	5	Abrams
GRSM_F_0174	Abrams Creek Below Cades Cove	35.591540	-83.853212	517.9	4	Abrams
GRSM_F_0489	Abrams Creek 300 m Below Trailhead Bridge	35.591686	-83.855501	516.6	5	Abrams
GRSM_F_0129	Pretty Hollow Creek at Log Bridge	35.662977	-83.135916	1166.2	2	Cataloochee
GRSM_F_0130	Onion Bed Branch (Cataloochee Cr)	35.671128	-83.138954	1260.7	2	Cataloochee
GRSM_F_0144	Palmer Creek Above Pretty Hollow Cr	35.639013	-83.130776	918.2	3	Cataloochee
GRSM_F_0147	Lower Cataloochee Creek	35.666872	-83.072724	750.5	5	Cataloochee
GRSM_F_0148	Lower Little Cataloochee Creek	35.669160	-83.072790	751.6	4	Cataloochee
GRSM_F_0149	Middle Cataloochee Creek at Bridge	35.646706	-83.075289	776.3	4	Cataloochee
GRSM_F_0293	Rough Fork at Caldwell House	35.621592	-83.116544	847.0	3	Cataloochee
GRSM_F_0493	Palmer Creek at Davidson Branch Trail	35.634586	-83.119500	872.2	4	Cataloochee
GRSM_F_0004	Lower Rock Creek	35.761200	-83.210579	627.2	3	Cosby
GRSM_F_0114	Cosby Creek at Log Bridge	35.747944	-83.200304	781.7	3	Cosby

Station ID	Station Name	Latitude	Longitude	Elevation (meters)	Stream Order	Stream System
GRSM_F_0137	Upper Rock Creek (Cosby Creek)	35.745731	-83.216084	844.1	2	Cosby
GRSM_F_0492	Camel Hump Creek Off Low Gap Trail	35.744519	-83.198661	837.3	1	Cosby
GRSM_F_0255	Deep Creek at 3820	35.590149	-83.428462	1166.2	2	Deep
GRSM_F_0256	Deep Creek at 3215	35.568432	-83.425603	978.3	3	Deep
GRSM_F_0259	Deep Creek at Campsite 58	35.515938	-83.424367	712.7	4	Deep
GRSM_F_0326	Deep Creek at Boundary	35.458325	-83.437919	546.6	4	Deep
GRSM_F_0INC	Indian Creek admin road past Laney Cemetary access road	35.48371	-83.41043	646.2	3	Deep
GRSM_F_0221	Hazel Creek Above Cascades	35.547508	-83.582360	1222.0	2	Hazel
GRSM_F_0222	Hazel Creek at 3400 ft.	35.534731	-83.602908	1030.9	3	Hazel
GRSM_F_0224	Hazel Creek Just Below Proctor Creek Confluence	35.530120	-83.620727	925.6	3	Hazel
GRSM_F_0310	Bone Valley Creek (Hazel Creek)	35.500246	-83.680299	694.4	3	Hazel
GRSM_F_0311	Hazel Creek Below Haw Gap Creek	35.493755	-83.688687	662.2	4	Hazel
GRSM_F_0479	Hazel Creek at Bridge Upstream of Campsite 86	35.474220	-83.722369	524.1	4	Hazel
GRSM_F_0480	Haw Gap Creek at Bridge Near Campsite 84	35.494846	-83.688966	668.2	3	Hazel
GRSM_F_0483	Sugar Fork Above Haw Gap Creek	35.499383	-83.694972	698.9	2	Hazel
GRSM_F_0484	Hazel Creek at Cold Spring Gap Trail	35.503386	-83.659343	749.6	4	Hazel
GRSM_F_0485	Walker Creek Above Hazel Creek Trail	35.522951	-83.631158	874.6	2	Hazel
GRSM_F_0013	Little River at Boundary	35.667583	-83.714551	334.9	5	Little (East Prong)

Station ID	Station Name	Latitude	Longitude	Elevation (meters)	Stream Order	Stream System
GRSM_F_0014	Little River Above Y	35.659898	-83.702136	351.6	5	Little (East Prong)
GRSM_F_0023	Lower Middle Prong Little River	35.657314	-83.709815	349.6	4	Little (East Prong)
GRSM_F_0024	Lower West Prong Little River	35.656840	-83.710240	350.3	4	Little (East Prong)
GRSM_F_0040	Little River at Old Road Gate	35.649792	-83.563242	705.2	4	Little (East Prong)
GRSM_F_0213	Goshen Prong Above Fish Camp Prong	35.598589	-83.567512	1010.7	3	Little (East Prong)
GRSM_F_0220	Double Springs Gap Shelter (TN side)	35.565932	-83.542745	1667.1	1	Little (East Prong)
GRSM_F_0LR4	Goshen Prong Just Off Goshen Prong trail	35.584200	-83.547200	1266.7	2	Little (East Prong)
GRSM_F_0047	Lower Cannon Creek	35.680536	-83.399509	747.6	2	Little Pigeon
GRSM_F_0048	Porters Creek at Gate	35.688147	-83.396684	655.7	3	Little Pigeon
GRSM_F_0052	Middle Prong Little Pigeon at Boundary	35.738501	-83.416039	416.9	5	Little Pigeon
GRSM_F_0371	Porters Creek off trail up manway at elevation 4023 feet	35.64203	-83.36984	1226.2	3	Little Pigeon
GRSM_F_0LP3	Porters Creek at 3254 ft just above Horseshoe Branch	35.66237	-83.38532	991.8	3	Little Pigeon

Appendix C: NDW Field Data Sheet

GRSM Noland Divide Study Site: Field Data Sheet/Checklist

Bi-Weekly Data Collection ---- Page 1 of 3

Date: _____ Field Crew: _____

Time in Field: Start: _____ AM/PM Finish: _____ AM/PM

General Weather: (rain, cloudy, clear, sunny): _____ Air temp. _____ °F

Rainfall: Approximate number of days since last precipitation over 0.1 inch: _____

Seasonal: Forest Cover Leaves (ON / OFF) Snow Cover (YES / NO) _____ inch depth

NE/SW STREAM SITES

S1. Water Quality Sondes

Initials: _____

Sonde data downloaded:

☐ NE

☐ SW

NE File Name: _____

SW File Name: _____

Successful sonde calibration:

☐ NE

☐ SW

• pH4 reading before calibration:

NE _____

SW _____

• pH7 reading before calibration:

NE _____

SW _____

• pH Sensor Response Factor:

NE _____

SW _____

• Conductivity reading before cal:

NE _____

SW _____

• Cond Sensor Response Factor:

NE _____

SW _____

Battery voltage reading:

NE _____ V

SW _____ V

Replacement battery voltage:

NE _____ V

SW _____ V

WQ sonde performance notes:

S2. Grab Samples (taken)

☐ NE

☐ SW

Initials: _____

• Bottles labeled **NE** and **SW** respectively

S3. H-flume Stage - Level Data Loggers

Initials: _____

Stage data downloaded:

☐ NE

☐ SW

NE File Name: _____

SW File Name: _____

Successful stage calibration:

☐ NE

☐ SW

-Flume depth measurement

NE _____ ft

SW _____ ft

-Stage recorder reading

NE _____ ft

SW _____ ft

Battery voltage reading:

NE _____ V

SW _____ V

Replacement battery voltage:

NE _____ V

SW _____ V

Level data logger performance notes:

S4. H Flumes Cleared of Sediment

☐ NE

☐ SW

Initials: _____

H-flume maintenance notes:

Sheet Checked: UTK _____

GRSM _____

Appendix C (continued): NDW Field Data Sheet

GRSM Noland Divide Study Site: Field Data Sheet/Checklist

Bi-Weekly Data Collection ---- Page 2 of 3

Date: _____ Field Crew: _____

OPEN SITE - PRECIPITATION / DEPOSITION COLLECTOR / WEATHER STATION

O1. Deposition Collector

Initials: _____

Collector lid position: ☐ Open ☐ Closed

Collector running properly: ☐ YES ☐ NO

Battery voltage reading: _____ V

Water Quality Sample (taken): ☐ YES ☐ NO

- Bottle labeled OS with field weight (kg)

Collector water bucket: field weight: _____ kg

Collector water bucket replaced: Time: _____ AM/PM

Deposition collector performance notes:

O2. Rain Gauge Measurement: _____ in Time: _____ AM/PM Initials: _____

Rain gauge maintenance notes:

O3. Weather Station

Initials: _____

Weather data downloaded: ☐ YES ☐ NO

File Name: _____

Tipping bucket clear of debris: ☐ YES ☐ NO

Weather station performance notes:

THROUGH FALL / SOILLYSIMETER SITE

TS1. Bear Fence Protection

Initials: _____

Battery voltage reading: _____ V

Fence output voltage: _____ V

Replacement battery: (Yes/No) _____ V

Fence output w/ new batt: _____ V

Bear fence maintenance notes:

Sheet Checked: UTK _____ GRSM _____

Appendix C (continued): NDW Field Data Sheet

GRSM Noland Divide Study Site: Field Data Sheet/Checklist

Bi-Weekly Data Collection ---- Page 3 of 3

Date: _____ Field Crew: _____

THROUGH FALL / SOILLYSIMETER SITE (continued....)

TS2. Throughfall Collectors

Initials: _____

Seasonal operation (# of buckets): ☐ Summer (N=10) ☐ Winter (N=2)

Sample weight: Bucket #1: _____ kg Bucket #2: _____ kg

Buckets collected _____ Summ/Wint Field Total = _____ kg

TF Funnels cleaned (n/a during winter): ☐ YES ☐ NO

Sample labeled *TF* with field weight (kg): ☐ YES ☐ NO

Throughfall collectors performance notes:

TS3. Soil Lysimeters

Initials: _____

FIELD USE: <i>X indicates = sampled; numbers indicate approx. volume collected in mL</i>					
Horizon	1	2	3	4	Horizon Composited (5)
<u>A</u> (413_)					
<u>Bw</u> (414_)					
<u>Cb</u> (415_)					
Overflow Volume					

Samples labeled with lysimeter ID and volume (mL): ☐ YES ☐ NO

Battery voltage reading: Vacuum Pump batt-1: _____ V Timer batt-2: _____ V

Replacement battery voltage: Vacuum Pump batt-1: _____ V Timer batt-2: _____ V

Timer setting: (in minutes): ON: _____ min OFF: _____ min

Soil lysimeter performance notes:

TS4. Soil Moisture Probes and Data Logger

Initials: _____

Soil moisture data download: ☐ YES ☐ NO Time: _____ AM/PM

File Name: _____ Battery life: _____ %

Soil moisture probe performance notes:

TS5. Throughfall Air Temperature Data Logger

Initials: _____

Temperature data download: ☐ YES ☐ NO Time: _____ AM/PM

File Name: _____ Battery life: _____ %

Temperature data logger performance notes:

Sheet Checked: UTK _____ GRSM _____

Appendix D: Water Quality Survey Field Data Sheet

Great Smoky Mountains National Park - Water Quality Survey

Route (CIRCLE ONE)	Cosby Creek	Cataloochee	Hazel Creek	Date: _____
	Little River/Abrams	Deep Creek	Little Pigeon	

Name (PLEASE PRINT) (TU members include chapter name)	# of Hours Worked (nearest hour) (INCLUDE DRIVE TIME!!)	Name	# Hours Worked
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

Sample ID***	# on sample bottle									
Time of Day	time sample was taken									
Water Temp.	nearest 0.5° C									
Cloud Cover	see below									
Stream Width	see below									
Stream Depth	see below									
Recent Precipitation	see below									
Forest Floor Condition	see below									
Canopy Condition	see below									

Cloud Cover 1 = no clouds 2 = partly cloudy to cloudy (no rain) 3 = light rain / mist 4 = steady rain 5 = heavy rain / down pour / thunderstorm 6 = snow	Recent Precipitation (in last 48 hours) 0 = no rain 1 = light rain (less than 1/4 inch) 2 = moderate rain (between 1/4 to 1 inch) 3 = heavy rain (greater than 1 inch) 4 = snow
---	---

Stream Width (1 meter ~ 3 feet) 1 = less than 1 meter 2 = 1 to 3 meters 3 = 3 to 10 meters 4 = greater than 10 meters	Forest Floor Condition 0 = no snow cover 1 = snow cover
--	--

Stream Depth 1 = less than 6 inches 2 = 6 inches to 1 foot 3 = 1 to 2 feet 4 = 2 to 4 feet 5 = greater than 4 feet	Canopy Condition 1 = full leaf 2 = some leaves (Spring) 3 = some leaves fallen (Fall) 4 = no leaves out
--	--

***The sample site location sheet may have EXTRA site numbers and locations for sites in your route which may NOT be included in your sample bottles. The extra site numbers and locations are left in the site location sheet, incase some of them get re-incoprprated into the routes!!

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 133/133470, September 2016

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