

Great Smoky Mountains National Park

2008 Water Quality Annual Report



**US Department of Interior, National Park Service
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**University of Tennessee – Knoxville
Department of Civil & Environmental Engineering**



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GRSM 2008 WQ Annual Report

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This report describes for water quality monitoring in the Great Smoky Mountains National Park for calendar year (CY) 2008 work accomplished under Amendment No. 7 to **Cooperative Agreement No. 1443-CA-5460-98-007** between the University of Tennessee and the U.S. National Park Service and also under the Southern Appalachian Cooperative Ecosystem Studies Unit CESU Host Cooperative Agreement No. H5000 04 5040 Task Agreement No. J5460 05 0067 Modification No. 4 between the U.S. National Park Service and the University of Tennessee - Knoxville.

TABLE OF CONTENTS

	Page
1.0 Introduction.....	1
1.1 <i>Noland Divide Watershed.....</i>	2
1.2 <i>GRSM Park-wide Stream Survey for Baseflow Water Quality Monitoring</i>	6
1.3 <i>GRSM Water Quality Program Annual Reports and Research Publications</i>	8
2.0 Noland Divide Watershed: 2008 Data Summary and Discussion	9
2.1 <i>Annual Precipitation Volume</i>	9
2.2 <i>Annual Deposition Rates for Chemical Constituents</i>	9
2.3 <i>Soil Water Chemistry from Lysimeters.....</i>	122
2.4 <i>Stream Water Chemistry</i>	125
3.0 Park-wide Stream Survey	177
3.1 <i>Water Chemistry Results</i>	177
3.2 <i>Synoptic Water Grab Samples With Respect to 303d Listed Streams and Block-Designed Watersheds</i>	209
4.0 Laboratory Analysis: Quality Assurance\Quality Control.....	244
4.1 <i>Ion Chromatography Quality Assurance\Quality Control</i>	244
4.2 <i>Inductively Coupled Plasma-Atomic Emission Spectrometry QA/QC Procedures.....</i>	265
4.3 <i>Ion Balance Computations</i>	30
4.4 <i>USGS Round Robin Results</i>	32
5.0 References.....	34
APPENDICES.....	37

LIST of TABLES

Table 2-1. Statistical summaries for pH and conductivity from the soil lysimeters.....	13
Table 2-2. Statistical summaries of the anion chemistry analysis from the soil lysimeters. All values are given in $\mu\text{eq/L}$	13
Table 2-3. Statistical summaries of the cation chemistry analysis on the soil lysimeters. All values are given in $\mu\text{eq/L}$.13Table 2-3. Statistical summaries of the cation chemistry analysis on the soil lysimeters. All values are given in $\mu\text{eq/L}$	13
Table 2-4. Summary of 2008 water chemistry in SW and NE streamlets of Noland Divide study site. All parameter values are given in $\mu\text{eq/L}$, expect for pH which are in pH units and conductivity in $\mu\text{S/cm}$	136
Table 3-1. Descriptive statistic of 1993-2008 median water quality values for 43 Park-wide stream survey sites. CV = coefficient of variation = standard deviation / mean.	18
Table 3-2. Descriptive statistics of 2008 median water quality values for the 43 Park-wide stream survey sites. Percent Difference = $(2008 \text{ average} - 1993\text{-}2007 \text{ average}) / (1993\text{-}2007 \text{ average}) \times 100\%$	19
Table 3-3. Symmetric block design	21
Table 3-4. Synoptic baseflow sampling sites in symmetric blocks	23
Table 4-1. IC QA\QC for the anions/cations in 2008.	25
Table 4-2. IC QA/QC sample checks using USGS standard solutions for 2008.....	26
Table 4-3. ICP-AES quality control check sample results (n=139)	27
Table 4-4. ICP-AES T-183 USGS standard reference sample results (n=138).....	28
Table 4-5. ICP-AES Blank (deionized water) sample results (n=138)	29
Table 4-6. ICP-AES replicate sample results (n=36)	30
Table 4-7. ICP-AES spike sample results (N=36).....	31
Table 4-8. 2008 ICP-AES detection limits	31
Table 4-9. Average ion balances for NWD NE and SE streams, OS precipitation, and throughfall.	32

Table 4-10. USGS Round Robin results. All concentration data are reported in ppm, and conductivity is given in $\mu\text{S}/\text{cm}$	33
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LIST of FIGURES

Figure 1-1. Location of Great Smoky Mountains National Park.....	1
Figure 1-2. Map of Noland Divide watershed showing water quality monitoring sites.....	4
Figure 1-3. Photos depicting wet deposition collection (right) and throughfall collection (left)...	5
Figure 1-4. H-flume weir on the NE stream, Noland Divide watershed.	6
Figure 1-5. Water quality monitoring sites for the GRSM Park-wide survey.....	7
Figure 2-1. Total annual wet-only and throughfall precipitation volumes received by the NDW.	10
Figure 2-2. Total annual inorganic nitrogen deposition entering the NDW as wet-only and throughfall precipitation.	10
Figure 2-3. Total sulfate entering the NDW as throughfall and wet-only precipitation.....	12
Figure 3-1. Synoptic baseflow sampling sites and 303d listed streams in the GRSM	21

1.0 Introduction

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

Since the 1980's national air quality monitoring has shown that the GRSM receives some of the highest rates of atmospheric deposition of acid pollutants in the United States (Shubzda *et al.* 1995; NADP 2006; Sullivan *et al.* 2007), which has been linked to emissions from regional coal-fired power plants (Chestnut and Mills 2005). Most of the GRSM streams are low in alkalinity (acid neutralizing capacity, ANC), and exhibit acidification (lowered pH) chronically and episodically (Robinson *et al.* 2005, 2008; Deyton *et al.* 2008). Watershed geology and soil cannot buffer the acid pollutants.

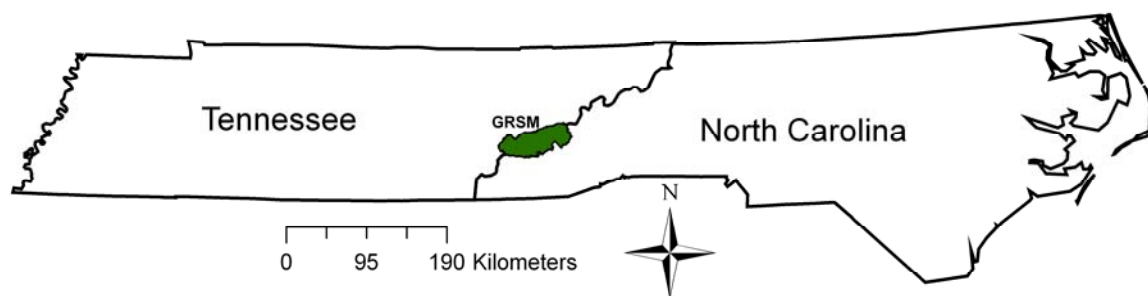


Figure 1-1. Location of Great Smoky Mountains National Park.

A major concern of stream acidification in watersheds that lack acid buffering capacity is the facilitation of soil release of aluminum and delivery to streams, in which monomeric aluminum can be highly toxic to fish (Baldigo and Murdoch 1997; Neff 2007).

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

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

1.1 Noland Divide Watershed

Noland Divide watershed (NDW) was selected for long-term monitoring because of its high-elevation location. In the eastern United States, high elevation watersheds with base-poor cation buffering capacity tend to be vulnerable to stream acidification from acid deposition (Hyer *et*

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

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

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

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

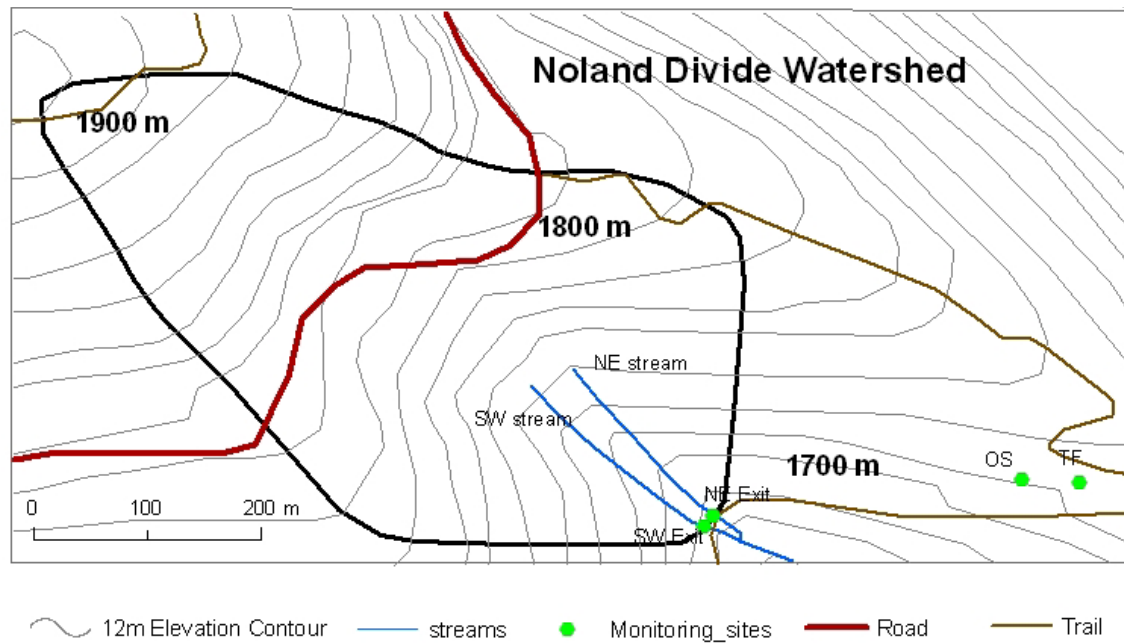


Figure 1-2. Map of Noland Divide watershed showing water quality monitoring sites.

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

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

buckets with LDPE liners are used only to collect precipitation. The collected water samples from OS and TF sites



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

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

Stream flow and water quality are measured at the watershed outlet for the southwest (SW) and northeast (NE) streams. Stream flows are estimated by use of H-flume weirs and GlobalWater® WL16 stage recorders installed at each stream (Figure 1-4). These WL16 recorders recently replaced originally installed float-cable devices with analog sensor in June 2007. Stage recorders measure flow depth every 15 minutes, and discharge is computed by H-flume standard formulas from the depth measurements. Water quality is continuously monitored with YSI600R® sondes (pH, conductivity and temperature), in which the SW sonde was installed in July 1991 and the NE sonde was installed in April 1998. Data from sondes are transmitted to a Campbell Scientific CR10X data logger recording data every 15 minutes. Stream water grab samples are collected from the NE and SW streams every two weeks and brought to the UT lab for chemical analyses (Section 4.0).

Soil water is collected by 12 ceramic suction lysimeters, four per three different soil horizons (A, Bw, Cb horizons). Lysimeters are located adjacent to the TF precipitation site. The volume of



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

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

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

Park-wide stream survey began in October 1993 to identify potential impacts of acid deposition on GRSM streams and monitor long-term changes in stream acidification (also termed long-term synoptic baseflow stream WQ monitoring). Sites were selected to assess the spatial variability of water quality within the GRSM across a range of elevations, geology types, and disturbance histories. From 1993 to 1995, samples were collected at 367 sites semi-annually. In 1995, the number of sites was reduced to 160, and samples collected on a monthly basis. In 1997, the number of sites was further reduced to 90, and samples collected quarterly (Figure 1-5). Data from the 1990's found 97% of the 90 sampling sites were classified as either sensitive, extremely sensitive, or acidic, classified by median ANC values less than or equal to 200 $\mu\text{eq/l}$ per liter (Harwell 2001). In addition, 77% of the GRSM sites were found with median pH values that can have adverse effects on aquatic organisms. The number of sites was further reduced in 2004 to 32 sites sampled bimonthly, and 11

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

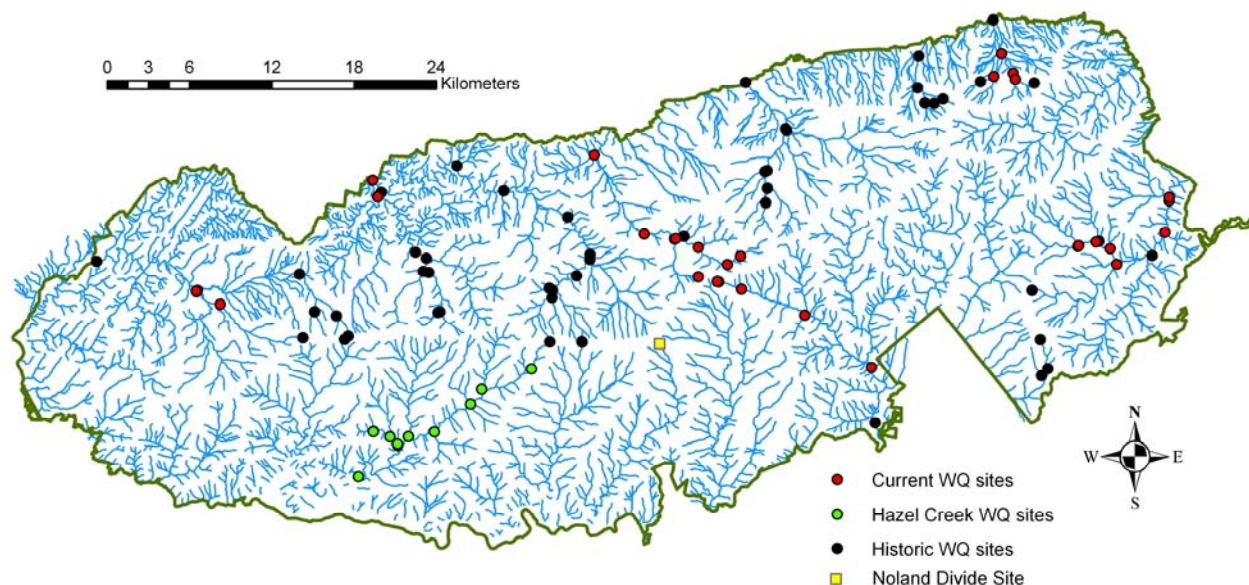


Figure 1-5. Water quality monitoring sites for the GRSM Park-wide survey.

From October 1993 to December 1998, water samples were collected and analyzed by personnel in the Department of Forestry, Wildlife, and Fisheries at the University of Tennessee - Knoxville. From January 1998 to the present, staff and students in the Department of Civil and Environmental Engineering have collected water samples and conducted the chemical analyses. The WQ parameters currently measured are pH, ANC, conductivity, sulfate, nitrate, ammonium, chloride, sodium, potassium, calcium, magnesium, aluminum, zinc, copper, iron, manganese, and silica.

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

significant decreasing time trends in pH and sulfate at lower elevations, but generally no long-term time trends in stream nitrate or ANC. If conditions remain the same and past trends continue, forecasting models suggest that 30.0 % of the sampling sites will reach pH values less than 6.0 in less than 10 years, 63.3 % in less than 25 years, and 96.7 % in less than 50 years.

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

1.3 GRSM Water Quality Program Annual Reports and Research Publications

Data summaries are generated annually for the GRSM water-quality monitoring program. Objectives of these annual reports are to detail and report results from the quality assurance/quality control (QA/QC) laboratory analytical protocols on samples collected, and to report and discuss basic trends found in the WQ data sets. Complete analysis and synthesis of the WQ data are conducted through periodic production of peer-review journal articles.

The WQ data in the annual reports and research publications are also used by other GRSM resource units including the air, species inventory, and vegetation units.

2.0 Noland Divide Watershed: 2007 Data Summary and Discussion

2.1 Annual Precipitation Volume

The annual rainfall amount collected during 2008 was 189.0 cm, 34 cm below the 17-year average for this site (Figure 2-1). Although the precipitation volume of 2008 was lower than most other years, this region showed the sign of recovery from the severe drought of 2007. The annual rainfall in 2008 was 23 cm higher than the annual rainfall in 2007.

2.2 Annual Deposition Rates for Chemical Constituents

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

During 2008, the estimated amount of total inorganic nitrogen entering the NDW from wet-only (OS) precipitation was 341.05 equivalents of nitrogen per hectare per year (N eq/ha/yr) and from throughfall was 939.75 N eq/ha/yr (Figure 2-2). In 2008, wet-only OS deposition was 154 eq/ha/yr *below* the long-term 17-year average, and the throughfall deposition rate was 263 eq/ha/yr *below* the 17-year average. Nitrogen rates at the TF site were greater than OS samples because the forest canopy collects airborne pollutants during dry periods. It should be noted that some foliar uptake of NH_4^+ and NO_3^- nitrogen constituents can occur in forested watersheds (Stachurski and Zimka 2002; Jin *et al.* 2006). Therefore, the difference between wet-only precipitation and throughfall inputs only represents a reasonable estimate of the dry plus cloudwater inputs to this watershed (Shubzda *et al.* 1995). The 2008 dry deposition rate for total inorganic nitrogen was estimated as 598.69 N eq/ha/yr.

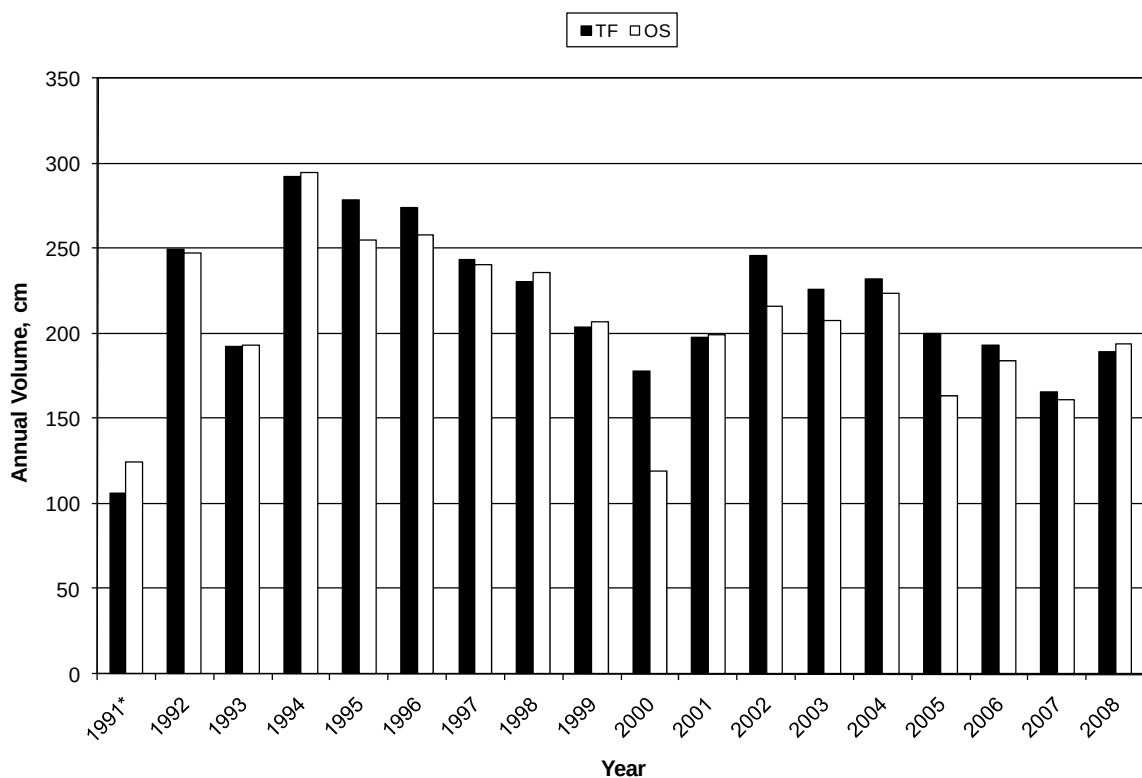


Figure 2-1. Total annual wet-only and throughfall precipitation volumes received by the NDW.

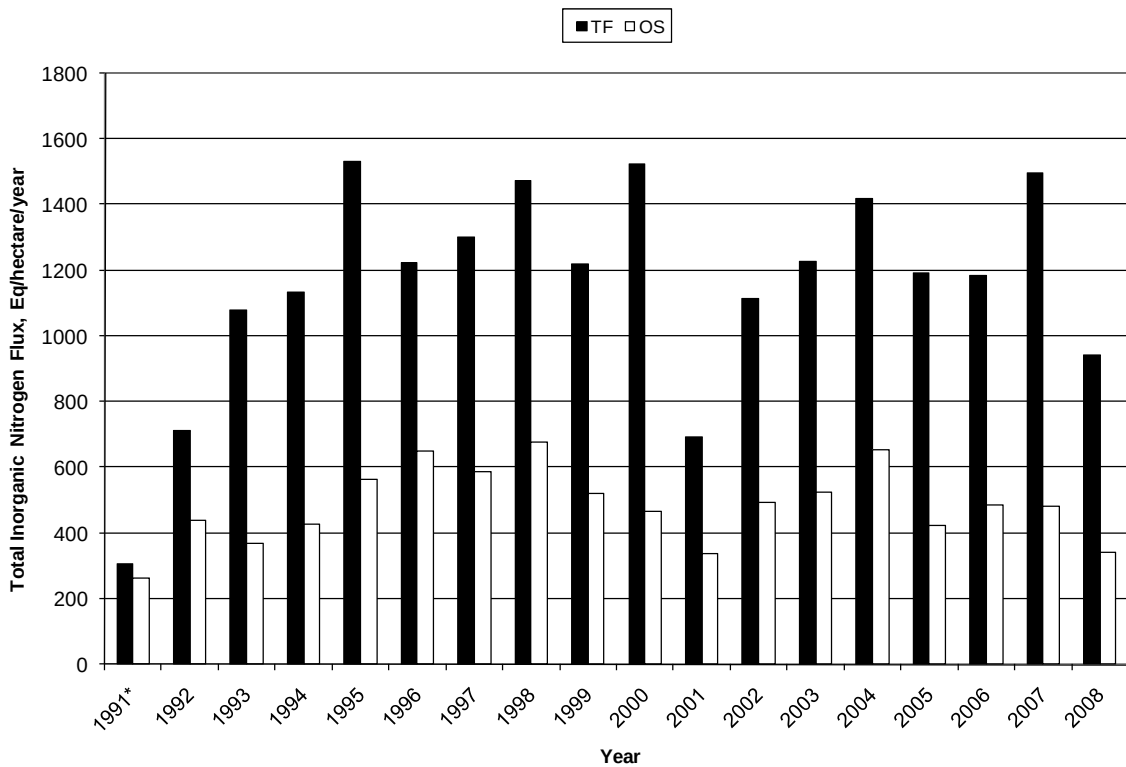


Figure 2-2. Total annual inorganic nitrogen deposition entering the NDW as wet-only and throughfall precipitation.

The estimated amount of sulfate entering the NDW from wet-only precipitation was 475.3 eq/ha/yr and throughfall was 1,297.5 eq/ha/yr (Figure 2-3). Wet-only deposition was approximately 94 eq/ha/yr *below* the 17-year average, and throughfall deposition was 506 eq/ha/yr *below* the 17-year average. The 2008 dry deposition rate for sulfate was estimated as 822.22 eq/ha/yr. Unlike nitrogen, sulfate flux represents a very good estimate of the total pollutant deposition rate that enters a watershed because foliar uptake and/or leaching are minimal (Garten *et al.* 1988; Lindberg and Garten 1988).

It should be noticed that both sulfate and total inorganic nitrogen deposition fluxes during 2008 were lower than most other years. In 1999, sulfate declined, but not total inorganic nitrogen. In 2001, total inorganic nitrogen declined, but not sulfate. Throughfall pH remained approximately the same for 1999 and 2001, approximately near 4.2. However in 2008 with apparently declines in both sulfate and total inorganic nitrogen, throughfall and wet-only deposition pHs were found to 4.75 and 5.64, which were significantly higher than the mean throughfall pH 4.17 and wet-only deposition pH 4.67 from 1991 to 2007. This observation may be a result of recent emission controls of SO₂ and NO_x at the TVA Kingston facility, or possibly a function of the recent prolonged drought. The 2009 data will help explain whether this is a new deposition trend, or a drought relationship.

A statistical analysis of the 17-year NDW data has been completed, and two manuscripts have been prepared for publication (Appendices B & C for the abstract, full version of the manuscripts are submitted in separate files). One paper focuses on mass balance of chemical constituent inputs and outputs currently has been accepted tentative on revisions in *Water, Air, and Soil Pollution*. A second paper focuses on long-term temporal trends, and it is under internal review by co-authors.

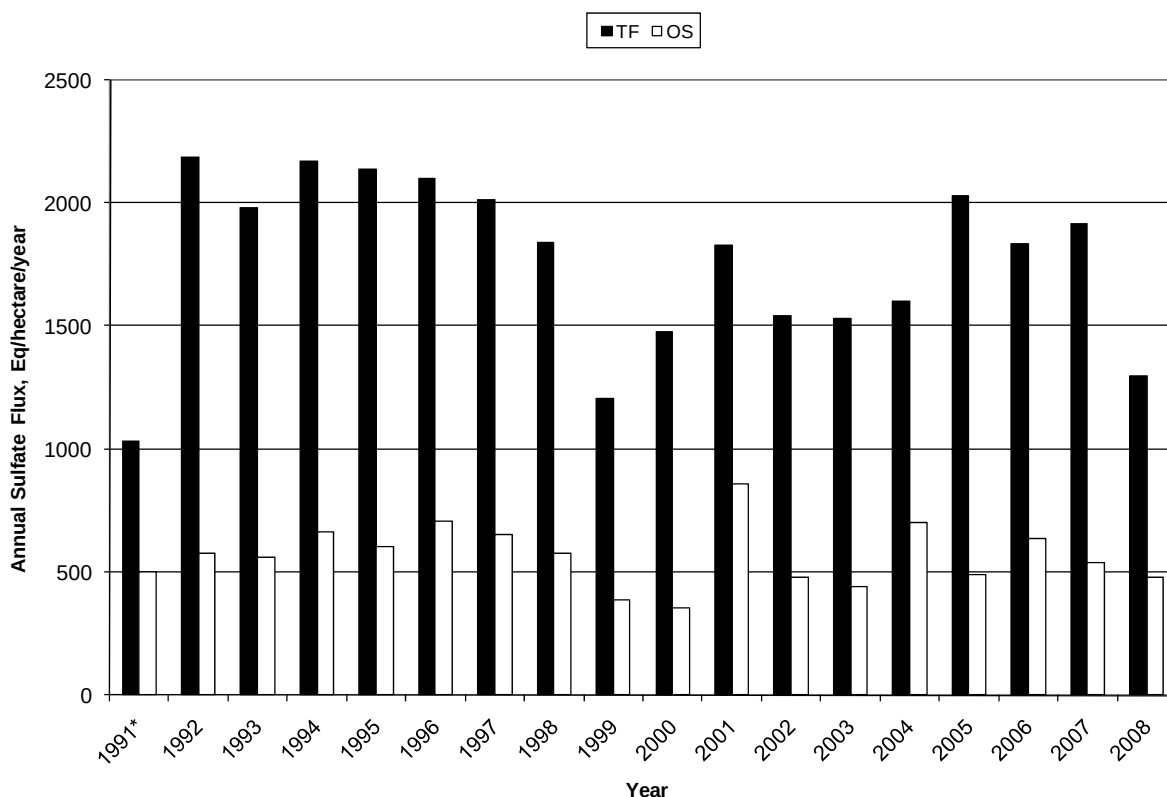


Figure 2-3. Total sulfate entering the NDW as throughfall and wet-only precipitation.

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

2.3 Soil Water Chemistry from Lysimeters

Soil water chemistry was collected monthly from 12 lysimeters, 4 located at 3 different depths for the NDW site (upper A horizon 8 cm; middle Bw horizon 35 cm; lower Cb horizon 65 cm). The annual volumes of water from the upper, middle, and lower lysimeters were 6,505 mL, 15,250 mL, and 13,320 mL, respectively. However, volumes can not be directly compared because of differential efficiency of lysimeters. Statistical summaries of the soil water chemistry for 2008 can be found in Tables 2-1, 2-2, and 2-3 (pH/conductivity, anions, and cations, respectively).

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

		pH	Conductivity, $\mu\text{S}/\text{cm}^2$
Upper Lysimeter	2008 Min - Max	3.82 – 4.45	26.00 – 76.90
	2008 Average	4.23	41.66
	1991-2007 Average	4.01	66.78
Middle Lysimeter	2008 Min - Max	3.81 – 4.59	24.80 – 75.90
	2008 Average	4.33	39.09
	1991-2007 Average	4.38	40.03
Lower Lysimeter	2008 Min - Max	4.43 – 4.66	26.10 – 39.20
	2008 Average	4.53	31.39
	1991-2007 Average	4.47	34.42

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

		Cl^-	NO_3^-	SO_4^{2-}
Upper Lysimeter	2008 Min – Max	12.99 – 35.59	7.01 – 107.50	71.17 – 114.69
	2008 Average	20.22	63.98	90.19
	1991-2007 Average	29.08	143.86	93.64
Middle Lysimeter	2008 Min – Max	9.72 – 41.71	1.54 – 92.92	54.86 – 141.50
	2008 Average	22.67	54.86	111.19
	1991-2007 Average	30.26	77.88	99.03
Lower Lysimeter	2008 Min- Max	13.18 – 30.76	37.68 – 89.57	90.63 – 115.89
	2008 Average	18.70	62.58	99.65
	1991-2007 Average	23.00	84.53	90.96

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

		Na^+	K^+	Mg^{2+}	Ca^{2+}
Upper Lysimeter	2008 Min - Max	14.11 – 32.00	4.89 – 38.07	10.08 – 21.76	9.23 – 37.68
	2008 Average	19.84	16.78	17.69	27.24
	1991-2007 Average	23.47	22.94	25.61	47.86
Middle Lysimeter	2008 Min - Max	13.03 – 33.10	4.98 – 41.49	9.45 – 25.08	9.63 – 37.54
	2008 Average	23.81	12.21	18.48	20.05
	1991-2007 Average	23.26	10.18	21.56	31.27
Lower Lysimeter	2008 Minimum	14.06 – 23.80	5.07 – 16.66	16.71 – 24.69	16.14 – 34.61
	2008 Average	17.72	10.28	19.60	26.26
	1991-2007 Average	20.21	9.45	25.28	37.28

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

Anion chemistry analysis (Table 2-2) found a decrease in chlorine and nitrate averages for 2008 compared to the 17-year averages. Chlorine concentrations for upper, middle, and lower layers decreased 8.86 µeq/L, 7.59 µeq/L, and 4.3 µeq/L, respectively. Nitrate concentrations for upper, middle, and lower layers decreased 79.88 µeq/L, 23.02 µeq/L, 21.95 µeq/L, respectively. The significant reduction of nitrate concentration in upper soil layer could be explained by the relatively low deposition fluxes of nitrate in 2008. Sulfate concentration was similar for the upper layer between periods, but concentrations increased approximately 10 µeq/L in the middle and lower soil layers between periods. If nitrification is reduced by lower nitrogen deposition and drier soils, soil pH will increase and thereby create a soil condition for sulfate desorption. In general, the high variability in soil sulfate concentrations is likely due differences in wet and dry samples periods, in which wetter periods the concentrations should be higher due to solute transport. This observation suggests that the recent reduction in sulfate and nitrate deposition may be changing the soil water chemistry.

The base cation chemistry remained relatively constant in 2008 compared to the 1991-2007 average, especially in the middle and lower soil layers (Table 2-3). However in the upper layer, sodium, potassium, magnesium, and calcium were found with lower concentrations, with calcium being reduced the greatest (about 20.62 µeq/L). A more detailed analysis of the soil water chemistry can be found in Cai *et al.* (Appendix B). Also, additional *in-situ* and laboratory experiments on soil

chemistry dynamics are in progress in order to help explain the observed NDW long-term trends.

Comparing the 2008 averages for soil water pH (4.23 upper layer, 4.33 middle layer, and 4.53 lower layer) to the 1991-2007 long-term averages, the pH increased significantly in the upper soil layer while remaining relatively constant for the middle and lower soil layers (Table 2-1). This may be explained in part by the observed increase in rainfall and throughfall pH, which would increase the pH of the uppermost soil layers first. In addition, a reduction in deposition inorganic nitrogen would also create the environmental condition to increase soil water pH in the upper layer by reducing nitrification rates. Reductions in base cations may also be directly linked to increases in pH in upper soil layer. The multiple possible biogeochemical processes involved with soil water chemistry can only be interpreted with long-term monitoring data. Changes in the deeper soils appear to be more dependent on hydrological pathways and heterogeneity of the physical soil matrix (Cai, *unpublished data*).

2.4 Stream Water Chemistry

Stream water quality is monitoring at the SW and NE streamlets biweekly (Table 2-4). Data for 2008 found average pH levels in the SW and NE streamlets to be 6.0 and 5.6, respectively. It appears pH has increased in the SW and NE streamlets from the long-term average (1991-2006) of 5.83 and 5.59, respectively. Long-term averages are from Cai et al. (*in review*; also see Appendix B). Stream sulfate levels were greater in 2008 compared to the long-term average 1991-2006. Sulfate in the SW and NE streamlets were 33.6 µeq/L and 44.8 µeq/L for 2008 compared to 29.4 µeq/L and 40.8 µeq/L for the long-terms averages, respectively. Calcium levels were less in 2008 compared to the long-term average 1991-2006. Calcium in the SW and NE streamlets were 44.0 µeq/L and 49.1 µeq/L for 2008 compared to 49.3 µeq/L and 54.1 µeq/L for the long-terms averages, respectively. Increased sulfate levels and increased calcium should lower the stream pH rather than increase it as observed.

However, nitrate levels were less in 2008 compared to the long-term average 1991-2006, which would infer that nitrogen deposition has a greater immediate influence on stream pH than sulfate deposition. Nitrate in the SW and NE streamlets were 29.8 µeq/L and 37.2 µeq/L for 2008 compared to 41.5 µeq/L and 46.6 µeq/L for the long-terms averages, respectively. Eventhough nitrate appears to immediately control stream pH, stream pH levels are a function of both cation and anion deposition, and the biogeochemical processes in the soil.

Table 2-4. Summary of 2008 water chemistry in SW and NE streamlets of Noland Divide study site. All parameter values are given in µeq/L, except for pH which are in pH units and conductivity in µS/cm.

Water Chemistry Parameter	SW Streamlet	NE Streamlet
pH	6.0	5.6
Conductivity	11.1	13.2
ANC	10.4	3.2
Cl	10.8	13.5
SO ₄	33.6	44.8
NO ₃ -N	29.8	37.2
NH ₄ -N	2.1	1.9
Na	23.3	23.9
K	9.5	11.2
Mg	17.8	20.6
Ca	44.0	49.1
Al	0.1	0.1

3.0 Park-wide Stream Survey

The Park-wide stream survey dataset for 2008 included samples from 32 sites collected during six stream surveys (January, March, May, July, September, and November); and 11 samples collected from the Hazel Creek watershed in April and August of 2008. As described in Section 1.2, park-wide surveys for stream water quality began in GRSM in October 1993 with 367 sites being sampled (Appendix D). Since 1993, reductions in the number of samples collected have occurred to optimize information for effort expended. Based on the results of Odom (2003) the number of sites was reduced to 43 sites in 2004. In this report, 2008 WQ data are summarized from the 43 current sites. In addition throughout the following text, comparisons will be made between the 2008 data and previous data collected from October 1993 through November 2007.

3.1 Water Chemistry Results

Descriptive statistics of the WQ constituents for the 1993 to 2007 dataset for the 43 survey sites are presented in Table 3-1 (minimum, maximum, mean, standard deviation, and coefficient of variation), in order to compare with current 2008 data. Note, trace metals analyses for Al, Cu, Fe, Mn, Si, and Zn began in August 2003. Examination of coefficient of variation (CV) values for constituents provides information on how variable each constituent is spatially and temporally over the GRSM. Stream acidity as measured by pH was found to range from 4.81 to 7.44, and did not vary to any great extent (CV = 0.070). However, ANC was found to vary widely ranging from -14.360 µeq/L to 1,013.11 µeq/L (CV = 1.905), which is likely due to differences in surficial geology, soils, seasons, and flow stage. Similarly, sulfate was found to be highly variable ranging from 14.722 µeq/L to 314.00 µeq/L (CV = 1.114), and calcium ranging from 32.60 µeq/L to 766.90 µeq/L (CV = 1.539). Again, the variability in the data across the Park is likely due to geology, soils, seasons and vegetation, and flow stage. Cades Cove area with the carbonate geology has the highest

concentrations in ANC, sulfate, and calcium, where concentrations of sulfate and calcium directly influence ANC. Metals typically were variable, but concentrations are low and wide changes would be expected depending on flow stage. Additional details on time trends can be found in Robinson *et al.* (2008), which authors conducted a temporal statistical analysis of this long-term data

Descriptive statistics of the median WQ values for the 2008 data are summarized in Table 3-2 (median refers to the 43 survey sites). In addition, Table 3-2 presents the percent differences between the 2008 medians and the average of 1993-2007 site medians. Most ion constituents for 2008 were

Table 3-1. Descriptive statistic of 1993-2007 median water quality values for 43 Park-wide stream survey sites. CV = coefficient of variation = standard deviation / mean.

Water Quality Parameter	Minimum	Maximum	Mean	Std. Deviation	CV
Median pH	4.809	7.440	6.372	0.444	0.070
Median ANC (µeq/L)	-14.360	1013.107	98.488	187.616	1.905
Median Conductivity (µS/cm)	10.655	96.300	20.212	17.021	0.842
Median Chloride (µeq/L)	9.487	20.564	14.431	1.978	0.137
Median Nitrate (µeq/L)	0.000	56.981	18.986	16.159	0.851
Median Sulfate (µeq/L)	14.722	314.003	45.752	50.985	1.114
Median Sodium (µeq/L)	17.855	67.250	39.342	9.689	0.246
Median Ammonium (µeq/L)	0.000	0.000	0.000	0.000	---
Median Potassium (µeq/L)	3.789	16.035	10.828	2.828	0.261
Median Magnesium (µeq/L)	16.251	182.829	41.749	36.182	0.867
Median Calcium (µeq/L)	32.603	766.900	97.338	149.847	1.539
Median Aluminum (ppm)	0.009	0.454	0.047	0.068	1.429
Median Copper (ppm)	0.000	0.050	0.003	0.008	2.229
Median Iron (ppm)	0.010	0.036	0.019	0.005	0.280
Median Manganese (ppm)	0.000	0.299	0.017	0.051	3.006
Median Silicon (ppm)	1.345	4.510	2.779	0.682	0.246
Median Zinc (ppm)	0.002	0.168	0.015	0.025	1.747

Table 3-2. Descriptive statistics of 2008 median water quality values for the 43 Park-wide stream survey sites. Percent Difference = (2008 average – 1993-2007 average)/(1993-2007 average) ×100%.

Water Quality Parameter	Minimum	Maximum	Mean	Std. Deviation	Percent Difference
Median pH	4.751	7.785	6.587	0.512	3.373
Median ANC (µeq/L)	-18.270	1192.482	108.351	224.685	10.015
Median Conductivity (µS/cm)	8.571	123.000	21.350	21.682	5.632
Median Chloride (µeq/L)	10.554	22.746	13.993	3.060	-3.032
Median Nitrate (µeq/L)	1.892	60.640	20.173	16.327	6.251
Median Sulfate (µeq/L)	14.767	342.045	50.720	56.058	10.858
Median Sodium (µeq/L)	18.805	69.137	39.821	9.172	1.217
Median Ammonium (µeq/L)	0.000	2.412	0.372	0.549	---
Median Potassium (µeq/L)	0.000	16.455	11.108	3.501	2.590
Median Magnesium (µeq/L)	16.318	220.291	43.159	41.746	3.378
Median Calcium (µeq/L)	26.644	959.035	102.943	179.511	5.758
Median Aluminum (ppm)	0.000	0.467	0.036	0.073	-22.845
Median Copper (ppm)	0.000	0.024	0.001	0.004	-81.206
Median Iron (ppm)	0.000	0.028	0.008	0.009	-59.886
Median Manganese (ppm)	0.000	0.262	0.007	0.040	-57.256
Median Silicon (ppm)	1.253	4.933	2.896	0.787	4.221
Median Zinc (ppm)	0.000	0.165	0.007	0.026	-52.563

less than 10% difference from the 15-year average, except for ANC and sulfate (+10.015%, and +10.858%, respectively). The difference percentage of ANC and sulfate are still very close to 10%. The increased concentrations observed in 2008 likely reflect that it was a drought year.

Dissolved metals are typically found in very low concentrations, thus minor median changes may cause percent differences between current and historical medians to be high (i.e., Al, Cu, Fe, Mn, Si, and Zn). The large percent differences in the dissolved metal concentrations are an artifact of their low concentrations, where a small change makes a large difference.

3.2 Synoptic Water Grab Samples With Respect to 303d Listed Streams and Block-Designed Watersheds

The Clean Water Act (CWA) was established to protect the quality of surface waters in the U.S., and includes regulatory and non-regulatory tools to reduce pollutant discharges into waterways, and manage polluted runoff. The primary goal of the CWA is to restore and maintain the chemical, physical, and biological integrity of surface waters in the U.S. to support the protection and propagation of fish, shellfish, and wildlife and recreation in and on the water. Clean Water Act, Section 303(d) requires states, territories, and authorized tribes to develop lists of impaired waters that do not meet water quality standards and develop Total Maximum Daily Loads (TMDLs). The pH standard for the State of Tennessee is a range between 6 and 9. A TMDL specifies the maximum amount of a pollutant that a waterbody can receive and still meet water quality standards, and allocates pollutant loadings among point and nonpoint pollutant sources. TMDLs must be developed within 8-13 years of impaired waters being listed.

In 2006, 67-km of 12 streams in the GRSM were listed on the 303d list as impaired due to low pH from atmospheric deposition and unknown sources (TDEC 2006; Figure 3-1). These streams were found with pH samples below 6. Of the 43 current synoptic baseflow grab sampling sites, three are collected in 303d listed streams: site 71 (Road Prong) and sites 4 and 137 (Rock Creek).

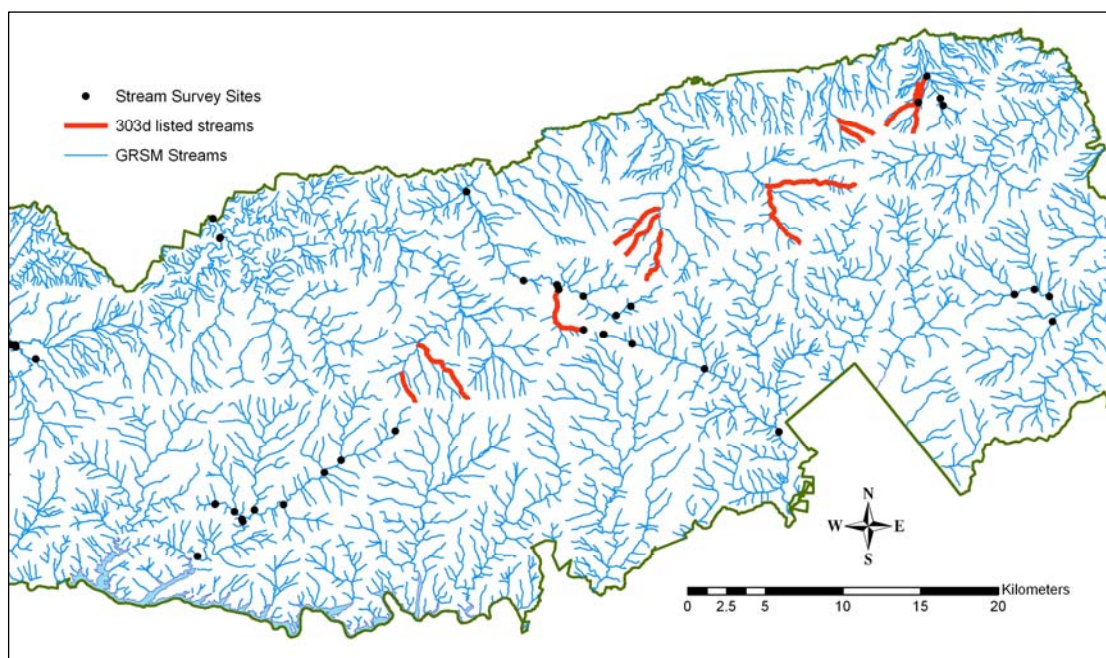


Figure 3-1. Synoptic baseflow sampling sites and 303d listed streams in the GRSM

The GRSM resource managers need to understand and predict the potential for impairment of aquatic resources by acid deposition throughout the park. It is essential to determine if acid deposition is the dominant mechanism of stream acidification in the GRSM and relate how acid deposition impacts stream water chemistry differently among GRSM watersheds related to basin characteristics. Additionally, it is important to understand the connection between baseflow and stormflow, and identify spatial relationships of stream chemistry. To develop appropriate critical loads, it is imperative to understand the watershed-scale processes associated with stream acidification, determine system responses to atmospheric deposition, and evaluate impacts to biota.

A symmetric block design was developed considering basin area, elevation, and Anakeesta presence/absence. Blocks are identified in Table 3-3. Watersheds in these blocks were delineated and detailed information has been accumulated for sub-watersheds in each block unit in ArcGIS 9.3.

Table 3-3. Symmetric block design by watershed factor: basin area, elevation, and presence/absence

of Anakeesta geology.

Block	Basin Area	Elevation	Anakeesta
1	< 10 km ²	< 1000 m	>10%
2	< 10 km ²	> 1000 m	>10%
3	< 10 km ²	< 1000 m	None
4	< 10 km ²	> 1000 m	None
5	10 km ² – 20 km ²	< 1000 m	>10%
6	10 km ² – 20 km ²	> 1000 m	>10%
7	10 km ² – 20 km ²	< 1000 m	None
8	10 km ² – 20 km ²	> 1000 m	None

Twenty-two synoptic baseflow grab sampling sites are located in six of the 8 block units (Table 3-4) except for blocks 4 and 8. However, two sites (143 - Lost Bottom Creek and 142 – Palmer Creek) are less than 100 meters downstream of these blocks 4 and 8. As such, water chemistry results from these sites could be considered for comparative block analyses. Stormflow sampling began May 2008 and was scheduled for a one-year monitoring project until June 2009. Data analysis and interpretation will follow in Keil Neff's dissertation.

Table 3-4. Synoptic baseflow sampling sites in symmetric blocks.

	Site ID	Site Stream Name	Block ID	Block Watershed Name
Block 1	221	Hazel Creek	237	Hazel Creek
	481	Little Fork	268	Sugar Fork
	482	Sugar Fork	268	Sugar Fork
	483	Sugar Fork	268	Sugar Fork
	485	Walker Camp Prong	236	Walker Camp Prong
Block 2	71	Road Prong	92	Road Prong
	234	Road Prong	92	Road Prong
	233	Walker Camp Prong	74	Walker Camp Prong
	237	Walker Camp Prong	74	Walker Camp Prong
	251	Beech Flats Prong	94	Beech Flats Prong
	252	Beech Flats Prong	94	Beech Flats Prong
	253	Beech Flats Prong	94	Beech Flats Prong
Block 3	4	Rock Creek	20	Rock Creek
	137	Rock Creek	20	Rock Creek
	114	Cosby Creek	23	Cosby Creek
	492	Camel Hump Creek	23	Cosby Creek
Block 4	143**	Lost Bottom Creek**	58	Lost Bottom Creek
Block 5	270	Beech Flats Prong	27	Beech Flats Prong
	480	Haw Gap Branch	42	Haw Gap Branch
Block 6	74	Walker Camp Prong	7	Walker Camp Prong
Block 7	142*	Palmer Creek*	49	Palmer Creek
	143*	Lost Bottom Creek*	49	Palmer Creek
	488	Mill Creek	24	Mill Creek
Block 8	142**	Palmer Creek**	8	Palmer Creek

4.0 Laboratory Analysis: Quality Assurance\Quality Control

Analytical procedures used to chemically analyze water samples for pH, gran ANC, conductivity, ions, and dissolved metals were based upon standard methods (Appendix E). WQ results for all samples are reported and archived in the NPSTORET database, however data quality is reported here. In 2008, 1084 water samples were analyzed. The total set of samples included 269 Park-wide Steam Survey samples; 150 Noland Divide samples; 263 samples for EPA and EPA/NPS joint projects; and 404 samples for Noland soil experiment.

In general, water samples collected in the field were transported to UT WQ laboratory located in the Science and Engineering Research Facility (SERF) building, and analyzed for pH, ANC, and conductivity within 24 hours. Analyses for pH, conductivity and ANC were conducted at room temperature to standardize results among many samples collected from different locations, times, and temperatures. After completion of these three analyses, water samples were refrigerated until the remaining analyses were performed (i.e., ions and dissolved metals). Because our analytical instruments and procedures are optimized for samples at low concentrations of dissolved constituents, dilution was only used when necessary for higher concentration sample constituents. All water quality analyses and data were checked by laboratory quality assurance\quality control (QA\QC) procedures, which are reported in the following sections.

4.1 Ion Chromatography Quality Assurance\Quality Control

Three anions (Cl^- , NO_3^- , SO_4^{2-}) and one cation (NH_4^+) were analyzed on the Dionex™ ion chromatograph (IC). The IC is fully automated, sending results to a computer with Dionex™ software in which computed concentrations are sent to an Excel spreadsheet file. Standard solutions were created with high-grade reagents and deionized (DI) water. DI water was tested for conductivity, and accepted conductivities were less than 1.0 $\mu\text{S}/\text{cm}$. In addition, standard curves produced by the

instrument were checked to insure a linearity of $R^2 > 0.9999$.

Developed to optimize the performance of the IC, several QA\QC procedures were performed including blanks (two for each batch), replicates (every 20 samples), spikes (every 20 samples), and check samples (USGS standard solutions; one for every 10 samples). Ion detection limits for ions on the IC are defined in Table 4-1. QA\QC results for blanks, replicates, and spikes are reported in Table 4-1, and results for USGS standard checks are reported in Table 4-2. QA\QC procedures indicated very good quality results for IC ions. Percent differences may appear high for low concentration constituents, but low concentration samples produce large % differences (e.g., SO_4^{2-} ; Table 4-2). Concentration differences were actually very small, near instrument detection limits.

Table 4-1. IC QA\QC for the anions/cations in 2008.

QA\QC Procedure	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+
Detection limits (DL, ppm)	0.01	0.07	0.01	0.006
Blank	not detected	not detected	not detected	< DL
Absolute average value in % difference in replicates	0.03% (n = 128)	0.66% (n = 127)	0.20% (n = 127)	0.71% (n = 65)
Average recovery in %	100.20% (n = 41)	100.78% (n = 41)	100.65% (n = 41)	99.84% (n = 46)

Table 4-2. IC QA/QC sample checks using USGS standard solutions for 2008.

Sample	Constituent	Number	USGS (ppm)	Avg. results (ppm)	% difference
N93	NH ₄ ⁺	168	0.195	0.190	-2.56
	NO ₃ ⁻	52	0.602	0.605	0.50
N94	NH ₄ ⁺	52	0.802	0.805	0.37
	NO ₃ ⁻	34	3.758	3.757	-0.03
N96	NH ₄ ⁺	102	0.834	0.835	0.12
	NO ₃ ⁻	128	5.049	5.047	-0.04
N97	NH ₄ ⁺	63	0.296	0.297	0.34
	NO ₃ ⁻	92	1.593	1.595	0.13
N100	NH ₄ ⁺	97	0.978	0.950	-2.86
	NO ₃ ⁻	43	3.118	3.109	-0.29
P47	Cl ⁻	334	3.63	3.635	0.14
	SO ₄ ²⁻	334	0.19	0.137	-27.89

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

Major cations (Na, K, Mg, Ca) and six trace metals (Al, Cu, Fe, Mn, Si, Zn) were analyzed on the ICP-AES. To ensure acquisition of high quality data, several ICP-AES QA/QC procedures were performed during measurement of cations and dissolved metals in the water samples from 2008. Standard solutions were prepared using certified ICP reagents and deionized (DI) water. Standard curves produced by the instrument were checked to insure linearity ($R^2 > 0.9999$) prior to sample introduction. Quality Control Check (QCC) samples, as part of our QA/QC protocols, were also

prepared from the certified reagents and DI, and run every 9 samples to ensure accuracy throughout the sequence. The results for the QCC samples are presented in Table 4-3.

An USGS trace metal sample was acquired to verify low concentration ICP-AES results and run every 9 samples. The most probable values were obtained from the USGS Standard Reference (<http://bqs.usgs.gov/srs/>) and compared to our ICP-AES results (Table 4-4). In table 4-4, note that copper had a high CV of 21.17%; however the USGS T-183 concentration for copper was below instrument detection limit. Percent errors in Tables 4-3 and 4-4 are the absolute value of the difference between mean and actual values divided by actual value multiplied by 100%. Note, CV (coefficient

Table 4-3. ICP-AES quality control check sample results (n=139)

Element	Mean (ppm)	Actual (ppm)	% Error*	Relative STDEV**
Aluminum	0.4977	0.50	0.46%	2.42%
Calcium	0.9992	1.00	0.08%	4.35%
Copper	0.4955	0.50	0.91%	1.87%
Iron	0.5030	0.50	0.60%	2.69%
Potassium	1.0113	1.00	1.13%	5.64%
Magnesium	0.9972	1.00	0.28%	2.56%
Manganese	0.5022	0.50	0.43%	1.78%
Sodium	0.4946	0.50	1.07%	4.16%
Silicon	1.0018	1.00	0.18%	2.03%

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

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

Zinc	0.4909	0.50	1.81%	2.43%
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Table 4-4. ICP-AES T-183 USGS standard reference sample results (n=138)

Element	Mean (ppm)	Actual (ppm)	% Error*	Relative STDEV**
Aluminum	0.1271	0.127	0.04%	4.20%
Calcium	11.6158	11.6	0.14%	3.22%
Copper	0.0036	0.0036	1.20%	21.17%
Iron	0.02025	0.206	1.67%	4.27%
Potassium	2.6156	2.57	1.78%	6.21%
Magnesium	7.8118	7.89	0.99%	1.98%
Manganese	0.0477	0.0492	2.98%	7.74%
Sodium	12.8471	12.7	1.16%	3.44%
Silicon	3.9000	3.87	0.78%	3.22%
Zinc	0.0862	0.0864	0.26%	3.19%

of variation) is the standard deviation divided by the mean, and represents a relative or normalized standard deviation among constituents.

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

Sample replicates were prepared and run every 20 samples on the ICP-AES (except for soil experiment water samples). The results are presented in Table 4-6. Measured values that fell below the instrument detection limits were not included in the analysis. This accounted for the discrepancy in the number of replicate samples analyzed and reported (Note: metals with low concentrations can

cause large percent errors for small variations in concentration). Sample spikes were also prepared and run on the ICP. The average percent recoveries are presented in Table 4-7. The percent recoveries of each element were all between 85% and 115% for each spike sample, which meets quality assurance standards. Minimum detection limits are determined annually. The current detection limits are shown in Table 4-8.

Table 4-5. ICP-AES Blank (deionized water) sample results (n=138)

Element	Mean Value (ppm)
Aluminum	.0022
Calcium	-.0085
Copper	.0002
Iron	.0016
Potassium	.0047
Magnesium	.0001
Manganese	-.0008
Sodium	.0032
Silicon	-.0037
Zinc	.0003

Table 4-6. ICP-AES replicate sample results (n=36)

Element	Median Absolute Percent Difference	n
Aluminum	6.47	29
Calcium	2.53	34
Copper	2.78	8
Iron	32.17	13
Potassium	16.96	24
Magnesium	0.91	36
Manganese	0.67	21
Sodium	2.46	35
Silicon	0.58	33
Zinc	1.22	23

4.3 Ion Balance Computations

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

Table 4-7. ICP-AES spike sample results (N=36)

Element	Average Percent Recovery
Aluminum	100.39
Calcium	100.25
Copper	99.58
Iron	97.78
Potassium	96.81
Magnesium	100.45
Manganese	101.26
Sodium	98.96
Silicon	101.60
Zinc	98.44

Table 4-8. 2008 ICP-AES detection limits

	2008 Detection Limits (ppm)
Aluminum	0.021
Calcium	0.05
Copper	0.012
Iron	0.012
Potassium	0.165
Magnesium	0.001
Manganese	0.002
Sodium	0.041
Silicon	0.019

Zinc	0.008
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QA/QC were excellent with only two sites out of a total 233 samples for the Park-wide stream survey exceeding an ion balance $\pm 15\%$. For the NDW samples, only two sample out of a total of 100 samples fell out of the $\pm 15\%$ range. These two samples are throughfall samples and have ion difference of -15.75% and -21.35% respectively. High organic acid concentration in throughfall samples was found to contribute the negative ion difference. Ion balances for NDW SW and NE streams, open sites and throughfall are summarized in Table 4-9. In NDW, ion balance differences for lysimeter samples were normally between +20% and +30%. For the lysimeter samples, high concentrations of aluminum contributed to the ion imbalance. The species calculation of aluminum at soil pH levels confirmed this finding.

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

	NE Stream	SW Stream	Open Site (OS)	Throughfall (TF)
% Ion balance	-2.69 %	-6.02 %	-2.11 %	-5.20 %
Absolute % Ion balance	4.60 %	6.44 %	4.90 %	10.31 %

4.4 USGS Round Robin Results

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

Although the USGS program is not a laboratory certification program, participation in this quality assurance exercise is mandatory for all laboratories providing WQ data for USGS sponsored reports. The USGS program provides the most probable values for the standard reference sample. Additionally, the USGS provides statistical Z-values and percent differences for each constituent in the reference sample. The most probable value, UT-value, statistical Z-value, and percent difference for each constituent are reported in Table 4-10. All reported values by the UT WQ Laboratory, except aluminum (T-191), copper (T-191) and sodium (P-49), had acceptable percent differences from the most probable value. However, concentrations of those three metals were close to the ICP detection limit (Table 4-8).

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

Sample	Analyte	MPV ¹	UT-results	Z-value	% difference
T-191	Al	0.155	0.152	-0.39	-1.94
	Ca	10.1	10.022	-0.21	-0.77
	Cu	0.00367	0.004	1.24	8.99
	Fe	0.430	0.430	0.00	0.00
	K	1.00	0.936	-1.02	-6.40
	Mg	3.30	3.308	0.05	0.24
	Mn	0.096	0.094	-0.36	-2.08
	Na	6.56	6.499	-.024	-0.94
	SiO ₂	4.83	4.727	-0.51	-2.13
	Zn	0.0463	0.047	0.30	1.51
P-49	Conductivity	13.5	12	-0.66	-11.11
	PH	6.17	5.91	-0.96	-4.21
	Cl	1.24	1.22	-0.28	-1.61
	SO ₄	0.6	1.99	0.17	0.50
	Ca	0.330	0.368	1.46	11.52
	Na	1.24	1.222	-.30	-1.45
N-100	NO ₃ ⁻ as N	0.761	0.76	-0.05	-0.13
	NH ₄ ⁺ as N	0.704	0.704	-0.18	-1.28

¹ Most Probable Value

5.0 References

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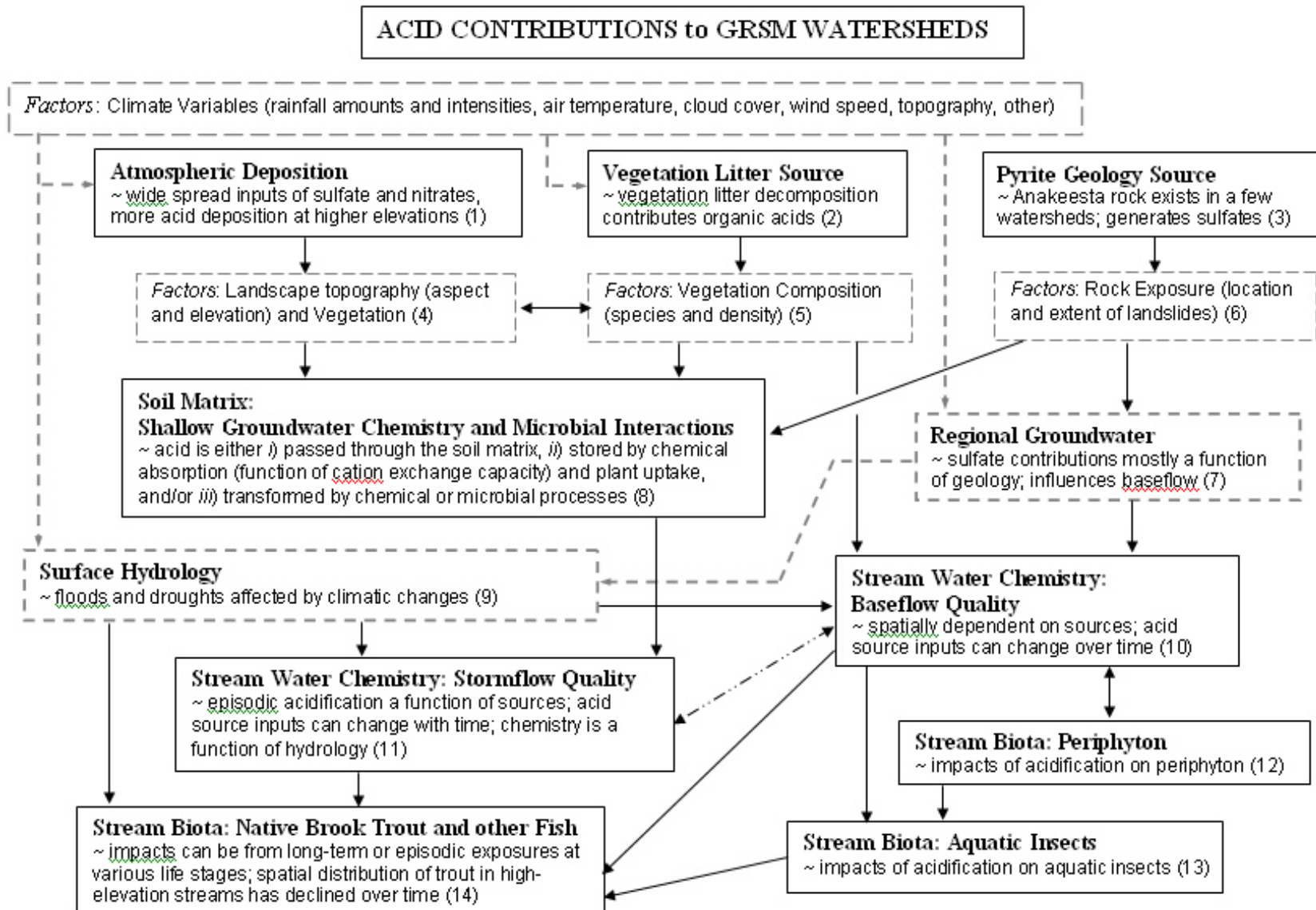
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APPENDICES

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



Appendix B: Long-term Effects of Acidic Deposition on Water Quality in a High-elevation Great Smoky Mountains National Park Watershed: Use of an Ion Input-Output Budget

Meijun Cai; John S. Schwartz; R. Bruce Robinson; Stephen E. Moore; Matt A. Kulp

Abstract

Impacts from acidic deposition on stream water quality in the Great Smoky Mountains National Park (GRSM) have long been reported, however a more complete understanding of the biogeochemical processes that regulate stream acidification is needed. Water quality monitoring of Noland Divide Watershed (NDW), a high-elevation watershed in the GRSM, was used to generate ion input-output budget in order to evaluate what processes have influenced stream pH and acid neutralizing capacity (ANC) over the long term. NDW was equipped with wet deposition, throughfall, soil lysimeters, and stream collection stations, and monitoring began in 1991 and continues to the present. Using data from 1991-2006 this study found high annual fluxes of SO_4^{2-} and NO_3^- deposition were inversely correlated with stream pH and ANC. Annual deposition fluxes of SO_4^{2-} and NO_3^- averaged 1,946 and 892 eq ha⁻¹ yr⁻¹, respectively. Data from NDW indicated that 60% of the SO_4^{2-} entering the watershed was retained, suggesting soil adsorption is a dominant biogeochemical process. Total inorganic nitrogen was retained 27% in NDW and 95% of NH_4^+ mass was converted to NO_3^- in the uppermost soil horizon, which suggests forest uptake and nitrification play key roles in regulating NO_3^- export. Mass export of base cations (Ca^{2+} , Mg^{2+} , Na^+), was observed, and apparently moderates stream acidification. Retention of K^+ was estimated at 31%, likely due to forest uptake. Stream export of Ca^{2+} was 963 eq ha⁻¹ yr⁻¹ compared to total deposition of 452 eq ha⁻¹ yr⁻¹. Long-term cation depletion from the NDW soils could limit recovery potential in stream water quality. Annual precipitation volumes were found correlated

with stream pH, ANC, SO_4^{2-} and NO_3^- suggesting that dominant biogeochemical processes differ between wet and dry years. Precipitation is a major driver to the observed stream acidification, and illustrates the importance of understanding potential impacts of climate variability on stream water quality. This unique long-term NDW study identified potential hydrological and biogeochemical processes regulating fate and transport of atmospheric deposition of acids in GRSM high elevation watersheds. This provides GRSM managers information that can be used to make informed decisions related to aquatic resources.

Key Words: stream acidification, acidic deposition; biogeochemical processes; input-output budgets, Great Smoky Mountains, critical loads, climate variability.

Appendix C: Long-term effects of acidic deposition on water quality in a high-elevation Great Smoky Mountains National Park Watershed: annual and seasonal patterns

Meijun Cai; John S. Schwartz; R. Bruce Robinson; Stephen E. Moore; Matt A. Kulp

Abstract

Evaluation of long-term and seasonal pattern of water chemistry in the Noland Divide Watershed (NDW), a high-elevation acidified watershed in the Great Smoky Mountains National Park (GRSM), is especially important to aid the Park management to predict the future water quality in response to the change in atmospheric deposition. Long-term biweekly monitoring deposition and stream water quality data from 1991 to 2007 in NDW were used for statistical analysis of temporal trend and seasonal variation. The deposition flux of sulfate and H^+ showed statistically significant decreasing trends, which was balanced by simultaneously decreasing precipitation volume and led to insignificant change of deposition concentration of sulfate. Sulfate concentrations in streams remained stable due to declining stream discharge and more than 50% retention of sulfate through this 17-year study period. For N compounds, the increasing deposition concentration of total inorganic nitrogen resulted in increasing throughfall nitrogen deposition. Because of increasing nitrogen retention, mainly caused by plant uptake due to recovery from balsam woolly adelgid (*Adelges piceae*), the stream export of nitrate showed declining trend. Stream nitrate concentration also showed significant seasonal pattern, with highest in winter and lowest in summer, due to seasonally varied hydrology and biological process as well as plant uptake. Despite the decreasing nitrate concentration, stream acidification recovery, reflected by increasing ANC and pH, was not observed in the NDW, possibly due to the depletion of base cations. Therefore, an acidification recovery of the NDW is anticipated to be delayed. Based on the analysis of temporal and seasonal

variation and combined with deposition chemistry, the regression models for stream pH, ANC, sulfate and nitrate were constructed.

Key Words: stream acidification, acidic deposition; temporal trend; seasonal variation; regression model; Great Smoky Mountains

Appendix D: Stream Survey Site Descriptions.

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

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

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

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

* The sites without end year are currently monitoring sites.

Appendix E: Analytical procedures for chemistry analysis performed at the University of Tennessee –Knoxville.

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

Standard Methods, AWWA (1995).