

Outline: Chapter 4 Natural Resource Conditions

4.3 Water Quality

4.3.1 Summary Condition/Trend Graphic and Measures

Resource	Indicator	Specific Measure	Status & Trend	Rationale and Reference Conditions	Notes
Water Quality	pH	pH Units		Tennessee State Water Quality Standard (TDEC, 2007): 6.0-9.0 & no change over 1 unit within 24 hrs)	
	Acid Neutralizing Capacity (ANC)	µeq/L		Tennessee State Total Maximum Daily Load Target (TDEC): 50 µeq/L	
	NO ₃ ⁻ , SO ₄ ⁻²	µeq/L		Spatial and temporal variations in local and regional data	
	Aluminum (Al)	µg/L		Local and national studies on biotic impacts: 0.2 µg/L (200 mg/L)	
	Metals (Cu, Mn, Zn)	µg/L		Tennessee Water Quality Criteria (TDEC, 2007) for freshwater systems	
	Temperature	Degrees Celsius		Tennessee Water Quality Criteria (TDEC, 2007) for freshwater systems: waters cannot exceed 20 °C.	
	Specific Conductance	µS/cm		Spatial and temporal variations in local and regional data	

4.3.2 Description/Background

4.3.2.1 Relevance

The landscape within the GRSM can be subdivided into 45 major watersheds (>5 km² in area) that contain over 3,380 km of stream channels (Parker and Pipes, 1990). Surface waters within the Park, including the hundreds of connected riparian wetlands which boarded its streams and rivers, are viewed as a critical ecological resource and a primary determinant of the Park's overall resource condition. Water quality in particular is considered an important ecological indicator; it was identified by the Park as the highest ranking Inventory and Monitoring Network category (vital sign) on the basis of ecological significance within the GRSM (NPS, 2011). Poor water quality can act as a significant ecological/biotic stressor, lead to ecological system deterioration, and negatively affect the recreational and aesthetic value of the region (Deschu and Kavanagh, 1986).

4.3.2.2 Threats and Stressors

Most streams within the GRSM originate within the Park boundaries; thus, the GRSM differs from many, if not most, other parks across the country in that its waters are not directly impacted by human development or agriculture (NPS, 2011). Stream waters are generally of high quality in terms of sediment loads and turbidity. In fact, the Tennessee Department of Environment and Conservation (TDEC) designated five GRSM watersheds as pristine. These five watersheds were recognized as containing Outstanding National Resource Waters.

The primary threat/stressor of concern, with regards to water quality, is atmospheric deposition of acid pollutants in the form of sulfur and nitrogen compounds that have the potential to lead to long-term (chronic) or episodic (flood related) acidification of surface waters (Weathers et al., 2006; Baumgardner et al., 2003; NADP, 2006). Air quality monitoring data collected since the 1980s have shown that the GRSM receives some of the highest levels of sulfate and nitrate deposition in the U.S. (e.g. Nodvin et al. 1995, Shubzda et al., 1995; Smoot et al. 2000, NADP 2006; Sullivan et al., 2007)(Figure 1), with the highest rates of deposition

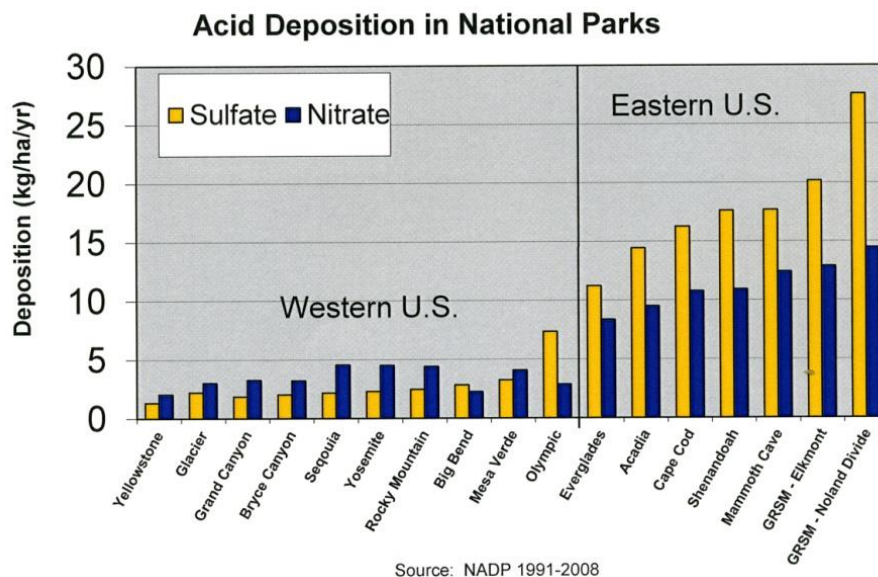


Figure 1. Average annual wet deposition of sulfate and nitrate in U.S. National Parks (from Vana-Miller et al., 2010).

occurring within high-elevation watersheds (Weathers et al., 2006). The acid pollutants are thought to be primarily derived from regional coal-fired power plants and vehicular traffic emissions (Chestnut and Mills 2005).

Surface waters throughout the eastern U.S. including the GRSM are particularly sensitive to acidification because the underlying bedrock contains limited concentrations of base metals and, therefore, lack the capacity to buffer the input of acid forming compounds to stream waters (Herlihy et al., 1991). Stream acidification has also been linked to exposures of the Anakeesta formation, a slate/phyllite containing sulfide minerals which underlies localized areas in the Park. Upon exposure to water and air the sulfide minerals (e.g., pyrite) are oxidized releasing protons (H^+), sulfate, and other metals to water bodies.

A closely linked concern to both chronic and episodic surface water acidification is the potential mobilization of toxic metals (e.g., aluminum, copper, lead, nickel, and zinc) from soils and sediments. Dissolved aluminum (Al), especially when occurring in the form of inorganic monomeric aluminum (Al_{IM}), is of particular concern in acidic waters (Driscoll et al., 1980; Driscoll 1985; Hermann et al., 1993; Baldigo and Murdoch, 1997). Monomeric aluminum has been shown to disrupt fish gill ion transport, and lead to the whole body loss of sodium, inhibiting ion regulation (Driscoll, 1985; Driscoll et al., 2001).

4.3.3. Measures

Eight measures were selected for this evaluation (listed below). They represent two parameters that allow for the characterization of stream water acidification (pH, ANC) and two measures of the primary drivers of acidification (sulfate, nitrate). Selected metals (e.g., Al) were also included in the evaluation as they may be mobilized in acidic surface- and groundwaters. The remaining measures, including specific conductance, and water temperature, are required parameters within the NPS Inventory and Monitoring Network, and provide an overall indication of the Park's water quality.

- pH (acidity)
- Acid Neutralizing Capacity (ANC)
- Sulfate
- Nitrate
- Aluminum
- Other Metals (copper, iron, manganese, zinc,)
- Temperature
- Specific Conductance

4.3.4 Reference Conditions

4.3.4.1 pH

At high concentrations, hydrogen ions (protons, H^+) as measured by pH can be lethal or cause sublethal physiological stress to aquatic biota (Baldigo et al., 2007; MacAvoy and Bulger, 2004; Woodward et al., 1991; Neff et al., 2009). In fish and macroinvertebrates, the primary affect of acid toxicity is the disruption of ion regulation which can lower blood pressure and lead to circulatory failure. Ion regulation is primarily disrupted in low pH waters by the interference of

Figure 2. Geologic map of the GRSM. The Park is primarily underlain by metamorphic rocks of the Ocoee Supergroup, which overlie Paleozoic sedimentary strata including carbonates of the Valley and Ridge province. Metamorphic isograds (kyanite, staurolite, biotite) show that the degree of metamorphism increases to the southeast (figure from Vana-Miller et al., 2010; figure modified from Southworth et al., 2005).

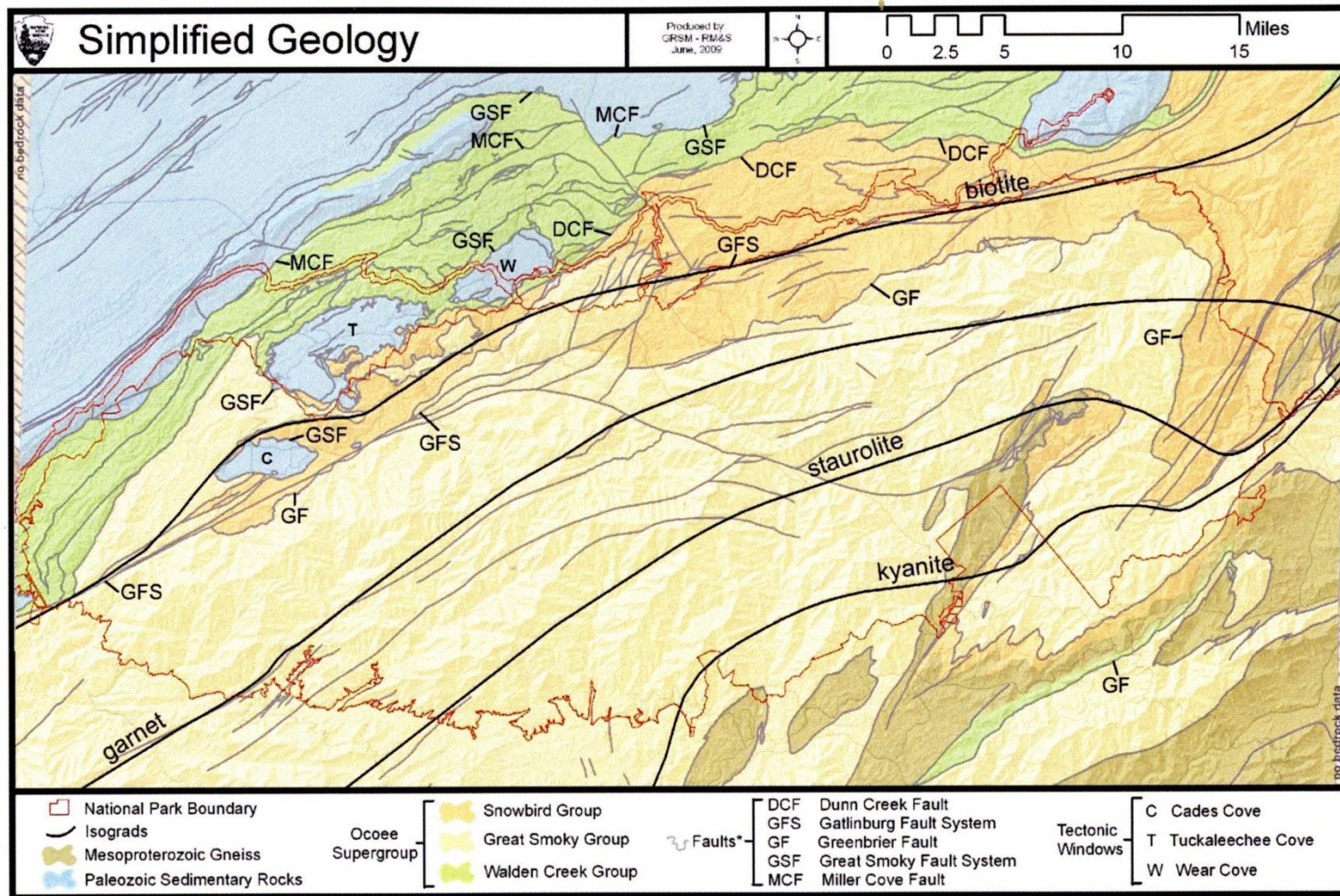
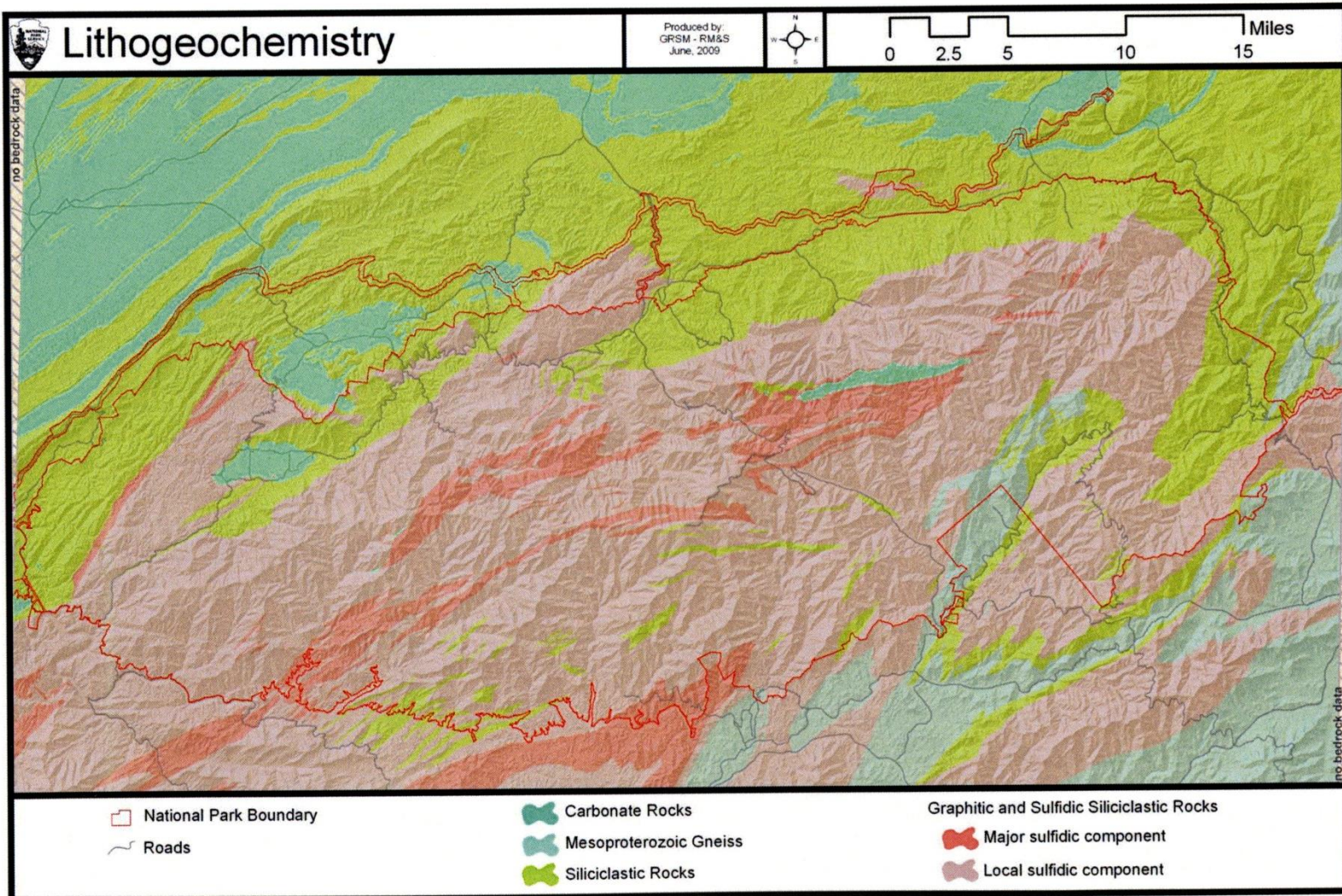


Figure 3. Lithogeochemical map showing the general distribution of rock types by their general geochemical composition. The Anakeesta formation is associated with the major sulfidic component. With the exception of the carbonate rocks, most rocks are low in base cations resulting in stream waters that are highly sensitivity to acidification (after Southward et al., 2004; figure from Vana-Miller et al., 2010).



protons with the gill transport system, resulting in a decline in sodium uptake and an increase in whole-body sodium loss (Grippe and Dunson, 1996; Neff et al., 2009). Evidence provided by Alabaster and Lloyd (1980) suggests that brook trout can survive episodic exposures to low pH waters (below 5) for short periods (< 24 hrs). Nevertheless, direct, lethal effects to fish can occur at pH values below about 5 (Neville and Campbell, 1988), even when exposure times are limited (see Cai et al., 2012a for a review of the effects of acidic waters on fish and macroinvertebrates). Amphibian survival also declines in low pH waters (below ~5.0), and some evidence suggests that both amphibian and salmonid egg production begins to decline at pH values below 7.0 (Sadinski and Dunson, 1992; Barnett, 2003). Table 1 by Baker et al. (1996) provides a classification of the potential effects of low pH waters on fish and other aquatic biota within stream of the northeastern U.S.

In addition to its direct effects on aquatic biota, low pH waters (<6.0) have the potential to increase the mobility, solubility, and toxicity of other toxic pollutants, particularly metals (Driscoll et al., 1980; Gensemer and Playle, 1999). For example, the fraction (concentration) of inorganic aluminum, which is toxic to fish, increases with increasing acidity, and is the predominant Al species in waters with a pH below 5.0 (Driscoll and Postek, 1995; Sullivan and Cosby, 1998).

The USEPA criterion to support freshwater aquatic life and sustain wildlife is set at a pH of 6.5-9.0 (USEPA, 1976). The acceptable, narrative standard set by North Carolina Department of Environment and Natural Resources is 6.0-9.0 (NCDENR, 2007). The Tennessee Department of Environment and Conservation also has set the water quality standard for pH in wadable streams at 6.0-9.0, but adds that there should be no change over 1.0 pH unit within a 24-hour period (TDEC, 2007, Chapter 1200-4-3). Herein, the utilized reference values are based on the Tennessee and North Carolina standards and set at 6.0-9.0.

4.3.4.2 Acid Neutralizing Capacity (ANC)

Acid Neutralizing Capacity (ANC) is widely utilized to characterize the acid-base chemistry of surface- and groundwaters. Essentially, ANC is the difference between proton acceptors and proton donors within a water sample. As such, it serves as an index of both the susceptibility of stream waters to acidification (Webb et al., 1989)(Table 2), and the extent to which stream waters have been acidified (Hemond, 1990). ANC is not affected by temporal variations in the total inorganic carbon content of the waters and, thus, is often regarded as a more appropriate indicator of the water's acidic condition (Hemond, 1990). Acid stream waters are defined as those in which $ANC < 0 \mu\text{eq/L}$.

Currently, state and federal standards for ANC do not exist. However, the Tennessee Department of Environment and Conservation has set a total daily maximum load (TMDL) management target at $50 \mu\text{eq/L}$. This TMDL target ($50 \mu\text{eq/L}$) is used herein as a reference value.

Table 1. Possible ecological consequences of acidic stream waters on biota within the northeastern U.S. (from Baker et al., 1996).

pH range	Biological Effects	Percentage of sample sites with median pH within range
>6.5	No adverse effects	23
6.0-6.5	Loss of sensitive benthic invertebrates	56
5.5-6.0	Loss of acid-sensitive fish Reduced reproduction insensitive fish species Increase in green algae in periphyton	13
5.0-5.5	Loss of most fish species Green algae dominate periphyton Loss of most mayflies, stoneflies, caddisflies and shellfish Reduced biomass and productivity	5
<5.0	Loss of all fish species Decreased nutrient cycling rates Decline in periphyton species richness Decline in benthic invertebrates Reproductive failure of acid-sensitive amphibians	3

Table 2. Summary of stream system sensitivity to acidic conditions (from Webb et al., 1989; based on studies of native brook trout in Virginia).

ANC range (µeq/L)	Classification	Percentage of sample sites with median ANC within range
< 0	acidic	4 to 5
0 - 50	Extremely sensitive	52
50 - 200	Sensitive	40
>200	Not Classified	3

4.3.4.3 Sulfate and Nitrate

Drinking water standards for sulfate and nitrate are 250 and 10 mg/L, respectively. However, within the GRSM the primary concern is the effect of sulfate and nitrate on stream water acidification. Their influence on acidification varies with a host of watershed parameters (e.g., geology, soil type and thickness, discharge and vegetation cover); thus, freshwater standards at the state or federal level do not exist. Perhaps the best approach to establish a reference value is through the use of geochemical modeling techniques aimed at setting a TMDL for sulfate and nitrate that will allow for the recovery of stream water to acidification; such efforts are currently underway. In the absence of established TMDLs, insights into sulfate and nitrate reference concentrations can be obtained by examining the observed variability in concentrations on a local and regional scale.

On a regional scale, the USGS (2011) characterized water chemistry, including sulfate and nitrate concentrations, within headwater streams along the Appalachian Trail (from Maine to Georgia). Median nitrate and sulfate concentrations for nine separate ecoregions vary from 2.39 to 11.2 mg/L and 0.063 to 0.330 mg/L, respectively (Tables 3, 4). Median concentrations within the GRSM for both constituents are relatively low in comparison to the median values calculated for these other ecoregions.

Sullivan et al. (2007) compiled sulfate and nitrate data from 66 watersheds in North Carolina, Tennessee, and South Carolina to calibrate a model used to assess stream water acidification. Sulfate values within these watersheds ranged from 9.6 to 207.4 $\mu\text{eq/L}$, whereas nitrate concentrations ranged from 0.0 to 23.1 $\mu\text{eq/L}$ (Table 5). Nitrate concentrations at the Coweeta Long-term Ecological Research Station, were less than 5 $\mu\text{eq/L}$ throughout the year, whereas sulfate concentrations were found to exhibit an annual volumetric mean of 12 $\mu\text{eq/L}$ (Hartman et al., 2009). Thus, both nitrate and sulfate values at Coweeta, which is generally characterized by thick soils, were observed to be on the low end of the concentration range cited by Sullivan et al. (2007) and the USGS (2011). In addition, the values at Coweeta are within the range of values observed in the Park, but are below the mean values calculated for data obtained from the 387 sites between 1993 to 2009 (Cai et al., 2012a). It follows then that while additional analyses are required to set reference condition, nitrate and sulfate concentrations similar to those are observed at Coweeta (5 and 12 $\mu\text{eq/L}$, respectively) serve as general reference values.

Table 3. Nitrate concentration in $\mu\text{eq/L}$ of headwater and adjacent streams of Appalachian National Scenic trail (data from Argue et al., 2011).

Ecological section	Number of catchments	Minimum	25th percentile	Median	75th Percentile	Maximum
White Mountains	6	0.42	0.48	1.11	1.77	9.03
Vermont–New Hampshire Upland	6	0.37	2.39	4.20	6.94	22.90
Green–Taconic–Berkshire Mountains	15	0.34	4.12	5.32	10.08	13.55
Lower New England	28	0.34	0.94	2.08	6.44	32.26
Hudson Valley	16	0.15	0.35	1.90	4.21	14.97
Northern Glaciated Allegheny Plateau	12	0.31	0.60	1.61	5.00	15.48
Northern Ridge and Valley	37	0.23	2.41	6.71	9.29	70.33
Blue Ridge Mountains	210	< 0.13	0.61	2.05	5.53	72.91
Allegheny Mountains	35	< 0.13	0.24	1.02	2.40	29.84

Table 4. Sulfate concentration in $\mu\text{eq/L}$ of headwater and adjacent streams of Appalachian National Scenic trail (data from Argue et al., 2011).

Ecological section	Number of catchments	Minimum	25th percentile	Median	75th Percentile	Maximum
White Mountains	53	43.10	69.12	83.28	95.980	158.86
Vermont–New Hampshire Upland	7	104.1	114.5	166.56	218.61	270.66
Green–Taconic–Berkshire Mountains	32	73.49	118.2	145.12	169.27	320.63
Lower New England	27	114.51	189.4	224.86	291.48	520.50
Hudson Valley	19	154.70	203.0	233.18	333.12	2311.0
Northern Glaciated Allegheny Plateau	12	84.52	125.5	139.70	160.73	249.84
Northern Ridge and Valley	40	23.94	102.9	137.20	226.94	1644.8
Blue Ridge Mountains	305	6.038	30.0	49.76	71.41	499.68
Allegheny Mountains	78	13.74	50.0	64.54	98.48	2883.6

Table 5. Observed stream water chemistry data cited by Sullivan et al. (2007) for streams in North Carolina, Tennessee, and South Carolina.

Site Name	Cal. Year	SO ₄ ²⁻ (µeq/L)	NO ₃ ⁻ (µeq/L)	Site Name	Cal. Year	SO ₄ ²⁻ (µeq/L)	NO ₃ ⁻ (µeq/L)	Site Name	Cal. Year	SO ₄ ²⁻ (µeq/L)	NO ₃ ⁻ (µeq/L)
Adam Camp Br.	2003	17.4	0	Indian Camp	2004	12.8	0.7	Scotsman Creek	2003	16.5	1.5
Bear Branch	2003	71.2	0	Indian Spring Branch	2004	23.7	2	South Fork Fowler Creek	2003	9.8	0.1
Bearpen Branch	2004	30.4	3.8	Kilby Creek	2003	10.4	0.7	Spivey Creek	2004	44.1	5
Beetree Branch	2003	123.6	0.1	Kirkland Cove	2004	31	11.3	Squibb Creek	1999	77.3	17.8
Big Cove Branch	2004	20.6	23.1	Left Prong South Toe River	2000	17.7	14.6	Stillhouse Branch	2005	33.5	0
Big Laurel Brook	2003	10.6	0.5	Lindy Camp Branch	1999	48	0.6	Unnamed creek A	2004	30.1	11.7
Big Oak Cove Creek	2004	38.1	11.1	Little Prong Hickey Fork	2000	21.4	6.3	Unnamed creek B	2004	45.4	16.9
Briar Creek	2005	55.3	1.2	Little Santetlah Cr. (NuCM site)	2000	32	6.7	Unnamed creek C	2004	27.9	18.3
Bubbling Spring Branch	2003	44.2	1	Long Branch	2000	11.8	0	Upper Creek	2003	33.3	6.1
Bubbling Spring West Tributary	2003	38.7	1.2	Lost Cove	2003	35.3	3.2	UT Flat Laurel Creek	2000	36	3.2
Buckeye Cove Cr.	2003	30.5	7.6	Lower Creek	2003	31.9	6.4	UT Laurel Branch	2004	74.1	5
Cane Creek Tributary	2003	36.7	2.4	McNabb Creek	2004	207.4	0.4	UT Linville River (NuCM site)	2004	52.7	1.2
Cathey Creek	2003	36	10.5	Middle Creek	2003	29.4	4.1	UT McNabb Creek	2004	20.3	0.5
Colberts Creek	2003	29.9	5.3	Mill Station Creek	2004	59.5	4	UT North Fork of Catawba	2005	38.4	0
Courthouse Cr.	2003	26.9	3	Paddy Creek	2005	48	0	UT Paint Creek	1999	45.5	8.8
Dark Prong	2003	27.9	0	Peach Orchard Creek	2000	50.3	20.1	UT Panthertown Cr. (Boggy Creek)	2000	31.3	1.2
Davidson River	2000	27.3	3.1	Pigpen Branch	2000	9.6	0	UT Russell Creek	2005	58.7	0
East Fork Pigeon	2003	21	2.2	Rattlesnake Branch	1999	39.3	0.5	White Creek	2005	48.4	0
Flat Laurel Cr.	2003	30	2.3	Right Hand Prong	2003	29.4	12.7	Wildcat Branch	2004	16.2	1.3
Glade Creek	2003	10.7	0.4	Roaring Branch	2000	35	21	Wilson Creek	2000	10.5	0.7
Greenland Creek	2003	28.6	1.8	Rough Ridge Creek	2000	26.9	1.8	Wolf Creek	2004	17.3	1.6
Indian Branch	2004	34	22.9	Russell Creek	2005	77.3	0	Yellow Fork	2005	48.5	0

4.3.4.4 Aluminum

The chemistry of aluminum (Al) in natural waters is complex as it can exist as free Al, or form a number of inorganic and organic complexes (species), depending on a wide range of parameters including pH, temperature, the dissolved organic carbon (DOC) content, and the concentration of other ions and ligands. The pH of the water acts as a particularly important control on its solubility and speciation (Driscoll and Postek 1996; Howells et al. 1983; Spry and Wiener, 1991). Aluminum is relatively insoluble under neutral pH conditions (6.0 - 8.0), but its solubility under acidic and alkaline conditions (pH <6 or >8), or where complexing ligands are present, is enhanced. Free Al and inorganic monomeric aluminum are considered to be the most toxic chemical forms to fish and other aquatic biota (Gagen and Sharpe, 1987b). Dissolved Al, particularly Al_{IM}, tends to disrupt ion transport within fish gills by replacing calcium on the gill surfaces (Dussault *et al.* 2004). Thus, dissolved Al may result in ion regulatory problems as well as respiratory issues associated with the coagulation of mucous on fish gills (Driscoll, 1985; Exley et al., 1991; Hermann et al., 1993; Cai et al., 2012a). The toxicity of Al is influenced by several factors, including the pH and dissolved organic carbon (DOC) content of the water. Calcium concentrations are also important as calcium is known to reduce the permeability of biological membranes and may therefore reduce ion losses and Al toxicity. The base cation concentration of the water (i.e., water hardness) may also influence the toxicity to biota. These external influences are important because toxicity thresholds may vary spatially between the watersheds in a region as a result of their overall water chemistry.

The USEPA Water Quality Criterion for freshwater (87 µg/L for chronic exposure and 750 µg/L for acute exposure) is based on a pH range of 6.5 to 9.0, and represents the total recoverable Al within the waters (rather than the dissolved Al concentration). Similarly, state criterion for dissolved Al do not exist. However, a number of investigators have defined water quality thresholds for trout and other fish species as well as macroinvertebrates. Based on a review of these studies, Cai et al. (2012a) suggested that toxic effects occurred in salmonids (trout) and benthic macroinvertebrates at a concentration of >0.2 mg/L (200 µg/L) for both total dissolved Al and inorganic monomeric Al. This value is consistent with the investigation by Neff et al. (2009) within the GRSM that found that southern brook trout suffered physiological stress during acidic runoff episodes when “preceding 24-h mean pH values of 4.88, 5.0, and 4.87 and corresponding 24-h time-weighted average Al_{TD} concentrations of 210, 202, and 202 µg/L were observed.” Thus, 200 µg/L is used here as reference value.

4.3.4.5 Other Trace Metals

A number of metals in addition to Al are toxic to aquatic biota and may affect water quality within the park. However, recent data have only been collected for four metals in addition to Al: Cu, Fe, Mn, and Zn. Less extensive data sets were developed for other metals, primarily before 1995, including arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), silver (Ag), and mercury (Hg). Table 6 below provides a comparison of the various water quality criteria that have been put forth for North Carolina, Tennessee and the USEPA for each of these metals. With the exception of Fe, the utilized reference values are based on the maximum and continuous water quality criterion provided by the Tennessee Department of Environment and Conservation (2007, chapter, 1200-04-03). Iron is based on the USEPA and North Carolina guideline.

Table 6. State and federal water quality standards for selected metals.

Metal	North Carolina (total recoverable) (µg/L)	Tennessee (µg/L)	USEPA (µg/L)
Arsenic (As)	50	340 (maximum); 150 (continuous) (for AsIII)	340 (acute); 150 (chronic)
Cadmium (Cd)	2	2 (maximum); 0.25 (continuous); for hardness of 100 mg/L	2 (acute); 0.25 (chronic); for hardness of 100 mg/L
Copper (Cu)	7	13 (maximum); 9 (continuous) (for hardness of 100 mg/L)	Based on Biotic Ligand Model which requires 10 input parameters (temperature, pH, dissolved organic carbon (DOC), calcium, magnesium, sodium, potassium, sulfate, chloride, and alkalinity)
Chromium (Cr)	50	570 (maximum); 74 (continuous); for Cr III at a hardness of 100 mg/L	570 (acute); 74 (chronic); for Cr III at a hardness of 100 mg/L
Iron (Fe)	1000	---	1000
Lead (Pb)	25	65 (maximum); 2.5 (continuous) (for hardness of 100 mg/L)	65 (acute); 2.5 (chronic); for hardness of 100 mg/L
Manganese (Mn)	---	---	---
Mercury (Hg)	0.012	1.4 (maximum); 0.77 (continuous)	1.4 (acute); 0.77 (chronic)
Nickel (Ni)	88	470 (maximum); 52 (continuous) (for hardness of 100 mg/L)	470 (acute); 52 (chronic) (for hardness of 100 mg/L)
Silver (Ag)	0.06	3.2 (maximum); for hardness of 100 mg/L	3.2 (acute); for hardness of 100 mg/L
Zinc (Zn)	50	120 (maximum & continuous) (for hardness of 100 mg/L)	120 (acute & chronic) (for hardness of 100 mg/L)

4.3.4.6 Specific Conductance

Specific conductance is a measure of the water's ability to conduct an electric current, and is usually reported in microsiemens per centimeter ($\mu\text{S}/\text{cm}$). It is closely linked to the concentration of ions in the water; the higher the concentration, the more conductive the water. For this reason, specific conductance is often used to assess the concentration of total dissolved solids, including pollutants, within water, and it provides an indicator of overall water quality.

Conductivity in uncontaminated rivers in the United States range from about 5 to 1,500 $\mu\text{S}/\text{cm}$. Due to this inherent natural variability, there are no state or federal water quality criteria for specific conductance. However, uncontaminated stream water within the southern Appalachians is typically below 50 $\mu\text{S}/\text{cm}$. Miller (unpublished data), for example, found that specific conductance within the forested Allen Creek watershed in Haywood County ranged from 12 to 22 $\mu\text{S}/\text{cm}$ between March 2007 and December 2011. Similarly, Webster et al. (2012) found that specific conductance within watersheds of the southern Appalachians, including the Coweeta Hydrologic Laboratory, ranged between 9.3 and 63.5 $\mu\text{S}/\text{cm}$, and exhibited a strong, indirect relationship with forest land-cover and a number of other variables used to describe development. Given the noted ranges for specific conductance, 50 $\mu\text{S}/\text{cm}$ is put forth here as a maximum reference value for predominantly forested watersheds in the Park.

4.3.4.7 Temperature

Temperature, or the intensity of heat stored within a body of water, is an important water quality parameter in that it (1) affects the solubility of oxygen and chemical pollutants in the water, and (2) influences metabolic oxygen demand and growth rates. Increases in water temperatures increase metabolic oxygen demand while reducing the dissolved oxygen content of the water. In general, chemical pollutants are also more soluble at higher temperatures.

Aquatic biota possess a range of water temperatures that they prefer and/or can tolerate. Above and below their health may suffer. In most instances, the primary concern is for increased water temperatures during the summer months in response to the input of warm water from anthropogenic sources, or the alteration of aquatic and riparian habitat (e.g., the removal of shade associated with the loss of stream side vegetation).

Table 7 below provides the water quality criteria set by the states of Tennessee and North Carolina. A reference value of 20 °C is used in this evaluation, which is consistent with both the Tennessee and North Carolina water quality criteria for trout streams.

Table 7. Tennessee and North Carolina Temperature water quality criterion.

Parameter	Tennessee	North Carolina
<i>Temperature</i>	The maximum water temperature change shall not exceed 3C° relative to an upstream control point. The temperature of the water shall not exceed 30.5°C and the maximum rate of change shall not exceed 2C° per hour. The temperature of recognized trout waters shall not exceed 20°C. There shall be no abnormal temperature changes that may affect aquatic life unless caused by natural conditions (TDEC, 2007)	Temperature: not to exceed 2.8 degrees C (5.04 degrees F) above the natural water temperature and in no case to exceed 29 degrees C (84.2 degrees F) for mountain and upper piedmont waters...the temperature for trout waters shall not be increased by more than 0.5 degrees C (0.9 degrees F) due to the discharge of heated liquids, but in no case to exceed 20 degrees C (68 degrees F)(NCDENR, 2007)

4.3.5 Data and Methods

4.3.5.1 Data

Water quality data within the GRSM have been intensively collected within the high-elevation Nolan Divide Watershed since 1991 (Figure 4). Beginning in 1993, these data have been complimented by the monitoring of water quality throughout the park as part of the Appalachian Highlands Inventory and Monitoring Network. Additional water quality data have also been collected within the Park, primarily before 1991, as part of specific and localized research investigations.

The high elevation Noland Divide watershed was initially selected as an Integrated Forest Study site in the 1980s for investigating the effects of acid rain on forest nutrient cycling, and to assess the response(s) of surface waters to acidic deposition. The watershed encompasses an area of 17.4 ha and ranges in elevation from 1680 to 1920 m. The sampling program includes the collection of waters associated with wet deposition, throughfall, soil waters (via lysimeters) and two headwater streams. Sampling began in July, 1991 and has continued to the present. With regards to stream waters, samples were collected weekly from 1991 to 2000, and bimonthly since 2001. Both stream water sampling sites were (are) equipped (lined) with an H flume and a stage recorder allowing for the calculation of discharge. Most samples have been collected during base flow. The samples are analyzed for pH, ANC, conductivity, acid anions (Cl^- , SO_4^{2-} , NO_3^-), ammonia (NH_4^+), and base cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+). With regards to the latter, Ca^{2+} and Mg^{2+} were not measured between 1993 and 1998.

The Inventory and Monitoring (I&M) Program was initiated in 1990 to (1) develop baseline data sets, (2) analyze and report on long-term data for a “modest” set of parameters, and (3) provide data and information on resource conditions to Park managers, planners, interpreters and other groups (Emmott et al., 2005). Inherent in this program was the intent to identify the potential impacts of acid deposition on GRSM stream waters (Vana-Miller et al., 2010). With regards to water quality, sampling began in 1993 with the establishment of the park-wide stream survey containing 185 monitoring sites located along GRSM streams (Figure 5). An additional 119 sites were added in 1994, followed by the addition of 53 sites in 1995 (Cai et al., 2012a). These 357 sites were selected to evaluate the spatial variability of water quality within the Park as a function of topography, geology, forest types, and disturbance history. They were monitored

semi-annually from October, 1993 to 1995. Since their initial establishment, the number and location of the monitoring sites have change as has the frequency of sampling (figs. 1, 2).

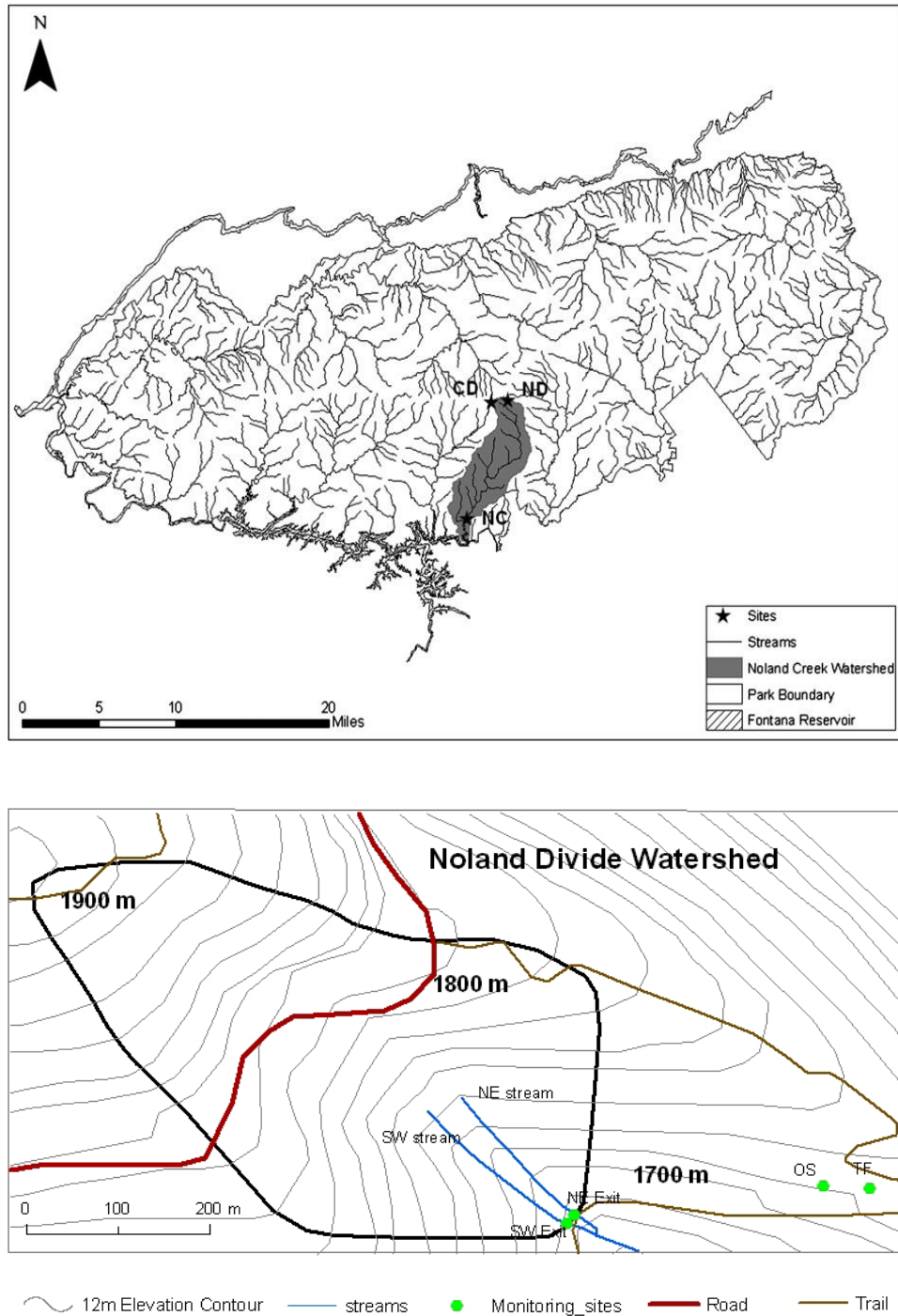
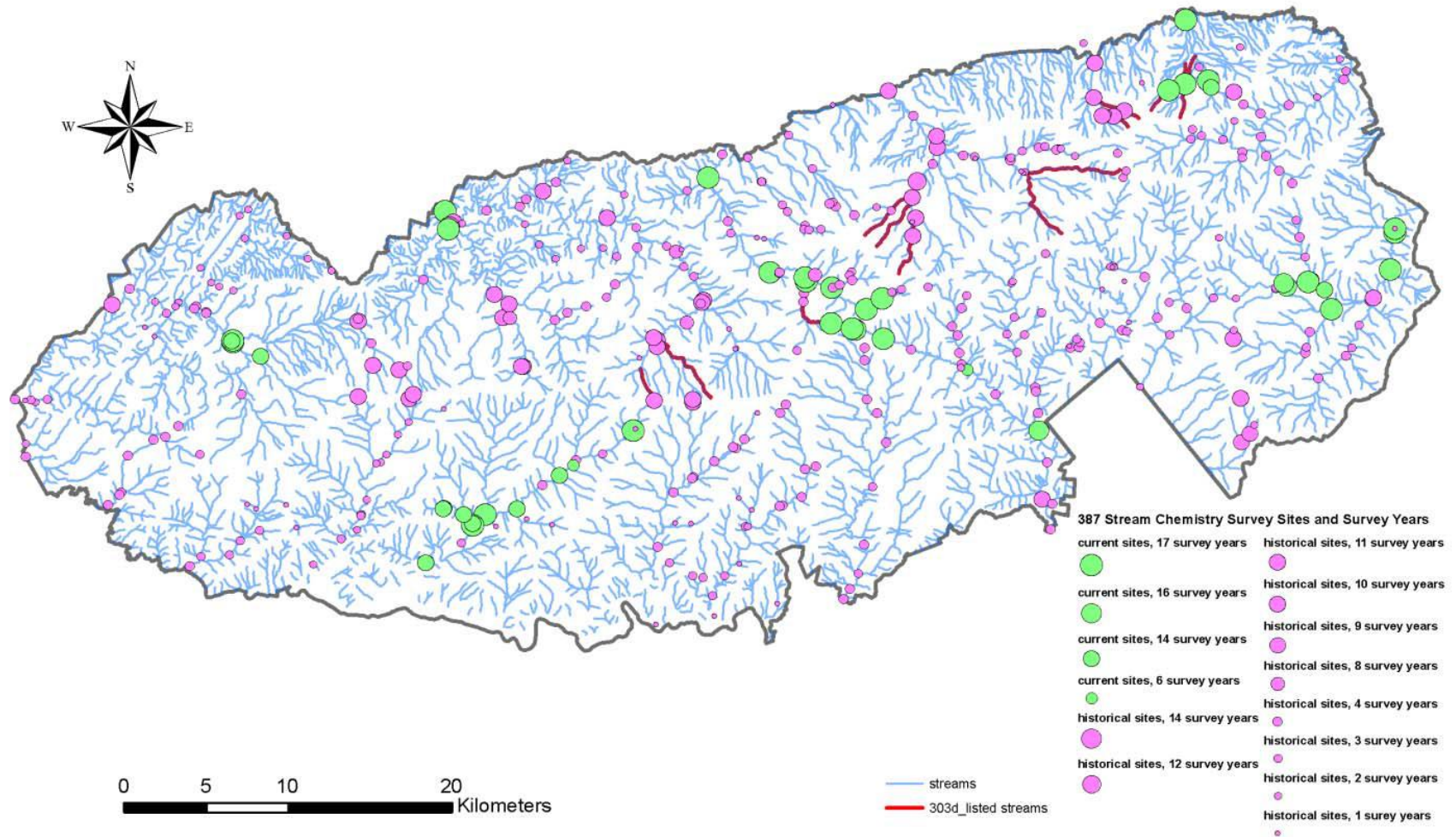


Figure 4. Location of Nolan Divide Watershed in the GRSM (top)(from Fisher and Wolfe, 2012); morphology of the Nolan Divide Watershed and location of the various monitoring sites (bottom).

Figure 5. Location of water quality monitoring sites within the GRSM since 1993 (From Cai et al., 2012a).



in 1996, data were collected monthly at 160 sampling locations, while in 1997 the number of sampling locations was reduced to 90 and data were collected quarterly (Cai et al., 2012a). In 2004, the number of monitoring locations was reduced to 43 sites located in 7 watersheds, 11 of which are located along Hazel Creek. Samples from these sites are collected biannually, and are thought to allow the use of base flow chemistry to characterize the health of most park surface waters and to determine statistical changes in water chemistry through time. A total of 27 sites have a complete record of monitoring data from 1993 to 2009. Sampling has primarily relied on grab samples without regards to stream flow conditions. Classification of stream flow as either base flow or storm flow has been conducted by some investigators on the basis of local precipitation records and adjacent USGS gaging station data. Collected water samples were analyzed for pH, gran ANC, conductivity, acid anions (Cl^- , SO_4^{2-} , NO_3^-), ammonia (NH_4^+), base cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+), and, from 2003 to present, selected metals including Al, Cu, Fe, Mn, Si, and Zn. The Inventory and Monitoring Program also included the collection of various biotic metrics (e.g., for fish and macroinvertebrates), although not all biotic monitoring sites are co-located with the water quality monitoring sites.

Some additional water quality data were collected prior to 1993 for sites within the Park and immediately adjacent to it. These data, summarized in NPS (1995), as well as more recent data collected throughout the Park, are available within the National Park Service's STORET (NPSTORET) database maintained by the NPS' Water Resources Division (WRD). Data are also available through the US Geological Survey National Information System.

4.3.5.2 Methods and Analysis

The eight measures of water quality can be subdivided into two categories on the basis of the degree to which they have been previously analyzed. These two categories include the following.

Group 1: Measures that have been extensively analyzed and the results of these analyses have been published in peer-reviewed scientific journals. This group includes pH, ANC, sulfate, nitrate, and aluminum as well as a number of other parameters (e.g., DOC) that are not included in our list of measures. Given the extensive analyses that have been previously conducted for these parameters, additional analyses were not conducted herein. Rather, the scientific literature describing the response of stream waters to acidification was reviewed, synthesized, and then compared to reference conditions to assess current and future resource conditions. The most significant studies with regards to these parameters are summarized in Appendix A.

Group 2: Parameters for which data exist, but which they have been less intensively analyzed. Data for a number of parameters (e.g., specific conductance, temperature, and some metal concentrations) exist, but have been less extensively analyzed. As for Group 1, a detailed review of the existing literature was carried out for these parameters. However, to gain a more in-depth understanding of their influence on water quality, basic statistical analyses were carried out to assess their current values within the Park, relative to existing reference conditions, along with any temporal trends that exist.

Flow	Statistic	pH	ANC ($\mu\text{eq/L}$)	NO_3^- ($\mu\text{eq/L}$)	SO_4^{2-} ($\mu\text{eq/L}$)	BCS ^a ($\mu\text{eq/L}$)
Base flow	<i>Median</i>	6.63	49.23	11.53	30.41	70.03
	<i>Mean</i>	6.52	68.27	16.12	37.58	88.69
	<i>Std</i>	0.57	104.72	15.39	29.77	117.27
	<i>Minimum</i>	4.44	-28.32	0.00	5.20	-45.30
	<i>Maximum</i>	7.88	1109.4	89.32	297.63	1081.20
Stormflow	<i>Median</i>	6.47	43.97	15.02	34.79	67.82
	<i>Mean</i>	6.41	57.86	18.20	43.12	80.41
	<i>Std</i>	0.60	78.11	16.25	35.76	85.94
	<i>Minimum</i>	4.39	-39.48	0.00	5.83	-112.44
	<i>Maximum</i>	7.75	706.43	87.22	361.51	733.00
a – base cation surplus (BCS) = [total base cations]-[anions]						

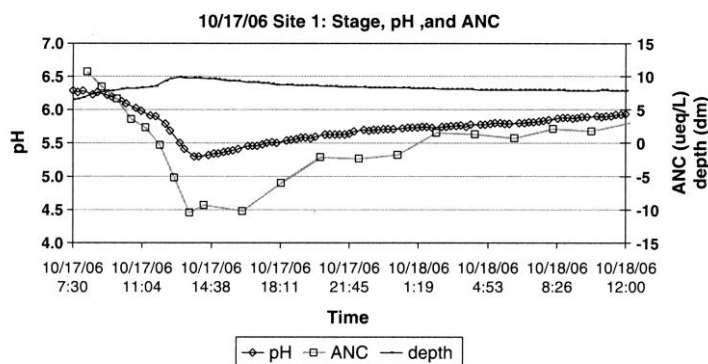
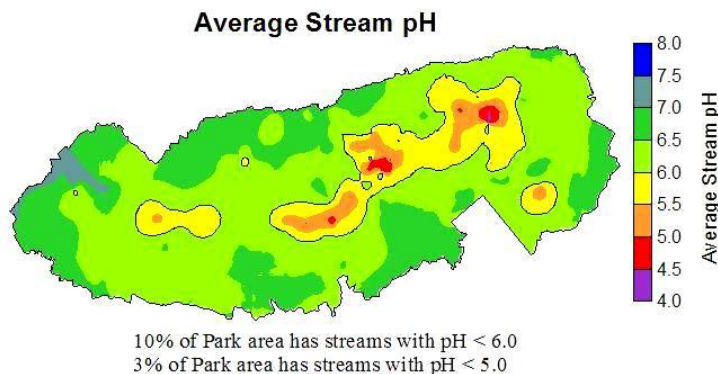


Figure 5. Typical change in stream water pH and ANC during a storm event as shown for the Middle Prong River M1 Site on 17 October, 2006 (from Deyton et al., 2009).

Figure 6. Modeled average stream water pH. The lowest pH values coincide with high elevation and the highest acid deposition rates. Approximately 50 to 60 % of Park streams exhibit an average pH of less than 6.5 (figure and results from NPS, 2010).



of acidification differ between sites and events, and not only include the influx of sulfate and nitrate associated with acid deposition, but the input of organic acids to streams waters. Base cation concentrations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) have been found to increase (Deyton et al., 2009) or remain constant (Cai et al., 2012a) during an event within the GRSM.

In light of the above, differences between base- and stormflow water chemistry (Table 8) can be attributed to the rapid flushing of the shallow soil layers of sulfate, nitrate, and organic acids as well as exchangeable cations, the latter of which serves as a buffer. The observed trends in base cation concentrations indicate that cation dilution is not the primary cause of the observed ANC declines (although cation dilution was noted at some sites, Deyton et al., 2009). Moreover, Deyton et al. (2009) found that the magnitude of the pH decline (at least within the three high elevation sites that they studied between March 2006 and May 2007) was related to both the magnitude of stormflow discharge and the length of the dry period between events. The authors interpreted the latter variable as an indicator of the amount of acid deposition that had accumulated over the landscape and within soil pore waters before sulfate and nitrate was flushed into adjacent channels, increasing their concentrations in stream waters.

Significant spatial variations in pH and ANC as well as sulfate and nitrate concentrations have been observed and modeled for both base flow and stormflow throughout the Park (Figure 6). These observed spatial variations in acid-base chemistry are dependent, in part, on the site's upstream watershed characteristics, including elevation, bedrock geology, soil type, hillslope gradients, and vegetation (Cooke et al., 1994; Cai et al., 2010; 2012a; Neff et al., 2012). The most severely impacted sites are predominantly located at elevations above ~198 m (4,200 ft). In general, stream waters collected at these high elevation monitoring sites during base flow exhibited lower pH and ANC, lower base cations, and higher nitrate concentrations compared to

lower elevation sites (Cai et al., 2012a; Neff et al., 2012). Cai et al. (2012a), for example, showed that park-wide, stream waters collected between 1993 and 2009 exhibited a decrease in pH and ANC at a rate of 0.32 pH units and -35.73 $\mu\text{eq/L}$, respectively, per 305 m (1,000 ft) of elevation gain. Decreases in pH and ANC with elevation have been attributed, in part, to elevated levels of acid deposition and higher volumes of precipitation at higher elevations (Cai et al., 2012a; Neff et al., 2012).

Basin size, a parameter closely related to basin elevation, also serves as a control on stream water acidification. In general, smaller basins ($<10 \text{ km}^2$) exhibited lower nitrate, sodium, and base cation concentrations during both base flow and stormflow conditions, and higher ANC and calcium concentrations during stormflow conditions (Neff et al. 2012a). Neff et al. (2012) argue that the noted trends with regards to basin size are related to the presences of thin, highly conductive soils on steep slopes that allow acid inducing ions to pass quickly through the soils to the channel during rainfall events. The reduced contact time between the interflow waters and the soils limits ion absorption and consequent buffering, and affects the retention, mobility and chemical processing of sulfate and nitrate in the soil (Neff et al., 2012; Cai et al., 2012a). The argument by Neff et al. (2012) is supported by the correlation of water chemistry to the hydraulic conductivity (Ksat) of the soil, such that soils with higher hydraulic conductivities were linked to lower pH, ANC, and base cation concentrations and higher nitrate, sulfate, and aluminum concentrations.

Bedrock type appears to act as an important control on pH and ANC within the GRSM. Catchments underlain primarily by sandstones (siliciclastics, Figure 3) were found to be the most sensitive to acidification, primarily due to their lack of base cations, while carbonate rocks tended to buffer the effects of acidification (Cai et al., 2012a). The latter (carbonate rock) are highly limited within the Park, although they were found to play a role in controlling stream water pH and ANC in Abrams Creek (Cai et al., 2012a). Thus, most basins within the GRSM are highly sensitive to acidification. Perhaps of more importance with regards to bedrock geology are exposures of the Anakeesta formation, a rock unit containing sulfide minerals (e.g., pyrite) that upon exposure to water and oxygen may be weathered (oxidized). The oxidation process releases hydrogen ions (H^+), sulfate, and trace metals into stream waters, while lowering pH. Neff et al. (2012), using an 8 block watershed study design that was thought to represent 77 % of the Park, showed that where the Anakeesta formation was exposed over at least 10 % of the basin, pH and ANC concentrations were lower and nitrate and sulfate concentrations were higher during base flow. In contrast, during stormflow, basins with the Anakeesta formation exhibited lower pH, Na and Al concentrations than basins where it was absent.

The potential biological effects of stream water acidification in the park have been examined by several investigators (Jackson, 2005; Neff et al., 2009; Cai et al., 2012a). Jackson (2005) found that trout biomass decreased with decreasing pH, ANC, and specific conductivity, and increased with increasing sulfate concentrations. Although sulfate concentrations were linked to the presences of the Anakeesta formation, in addition to acid deposition, the observed correlations suggest that acid deposition negatively impacts trout populations in the GRSM.

Neff et al. (2009) found in high elevation watersheds (i.e., those most affected by acidification) that (1) whole-body sodium concentrations in southern brook trout declined by 10 to 19 %

during storm events from March 2006 to May 2007, and (2) whole-body sodium concentrations were statistically correlated with elevated H^+ and Al_{TD} concentrations so that sodium losses were greater during more acidic conditions. Sodium loss in other studies has been shown to lead to fish mortality or chronic sublethal stress. Thus, the investigation suggests that the southern brook trout within high elevation watersheds may undergo acid-induced, physiologically stress. This distress may account, at least in part, for the current geographic distribution of southern brook trout within the GRSM.

The work by Neff et al. (2009) was subsequently supported by a more extensive examination of the biological effects of acidification by Cai et al. (2012a). Data analyzed during this latter study found: (1) a lack of fish within stream waters where $ANC < 0 \mu eq/L$, (2) YOY and adult trout density and biomass that was lower along stream reaches where $pH < 6.0$ than where $pH > 6.0$, (3) eight stream sites that should have been occupied by either brook and/or rainbow trout, but did not contain either, potentially as a result of stream water acidification, and (4) YOY brook and rainbow trout densities that were inversely correlated with dissolved aluminum concentrations. The fact that this latter trend did not hold for adults suggests that YOY may be more vulnerable to toxicological effects of high dissolved Al concentrations (discussed below) that accompany acid waters.

The data presented above show that because of the spatial and temporal variations in pH and ANC that occur, it is difficult to make generalizations regarding stream water acidification on a park-wide basis. Nonetheless, when combined with the available biological data, the fact that pH and ANC are locally below the utilized reference values indicates that stream water acidification is a significant concern within the GRSM. This is supported by the listing of 12 stream reaches on the 303d list as a result of low pH values (Table 9).

4.3.7.1.2 Temporal Variations

Water quality data collected since the early 1990s has made it possible to examine decadal-scale temporal variations in pH and ANC as well as sulfate, nitrate and base cation concentrations within the GRSM. Analyses of such temporal trends have focused on data from the high elevation Nolan Divide Watershed, or from all of the monitoring sites within the Park.

Within the Nolan Divide Watershed, the pH of throughfall, wet deposition, and stream waters did not change over time on a monthly volume-weighted basis, maintaining values of approximately 4.3, 4.7, and 5.8, respectively (Cai et al., 2011). Note that these values are all below the lower pH reference value of 6.0 pH units. Sulfate concentrations also remained constant at $30 \mu eq/L$, as did base cation concentrations. In contrast, monthly volume-weighted nitrate concentration in throughfall increased over the monitoring period by approximately $1.24 \mu eq/L/yr$, whereas concentrations and fluxes of nitrate significantly declined in stream waters by $0.56 \mu eq/L/yr$ and $139.56 \mu eq/yr$, respectively. In total, inorganic nitrogen was found to be exported before 1999, but has been retained within the watershed ever since. Cai et al. (2011) suggest that the increase in nitrogen retention reflects forest regrowth following the die-off of Frazer fir in the 1970s that resulted from the balsam wooly adelgid infestation.

Table 9. List of twelve 303 (d) listed streams within the GRSM (Tennessee Department of Environment and Conservation, 2008; table modified from NPS, 2010).

Waterbody ID	Impacted Water Body	County	Miles Impaired	Cause/TMDL Priority	Pollutant Source
TN06010106 004-0500	Rock Creek	Cocke	2.90	Low pH/ high	Undetermined
TN06010106 004-0610	Inadu Creek	Cocke	2.66	Low pH/ high	Undetermined
TN06010106 004-0810	Otter Creek	Cocke	1.52	Low pH/ high	Undetermined
TN06010106 004-0820	Copperhead Branch	Cocke	1.13	Low pH/ high	Undetermined
TN06010107 007-0700	Buck Fork	Sevier	3.8	Low pH/ high	Undetermined
TN06010107 007-0900	Eagle Rocks Prong	Sevier	6.4	Low pH/ high	Undetermined
TN06010107 007-1120	Shutts Prong	Sevier	4.79	Low pH/ high	Undetermined
TN06010107 007-1130	Lowes Creek	Sevier	2.22	Low pH/ high	Atmospheric Deposition - Acidity
TN06010107 007-1140	Cannon Creek	Sevier	3.72	Low pH/ high	Atmospheric Deposition - Acidity
TN06010107 010-1100	Road Prong	Sevier	4.6	Low pH/ high	Undetermined
TN06010201 032-0510	Goshen Prong	Sevier	6.66	Low pH/ high	Undetermined
TN06010201 032-0700	Unnamed Trib to Fish Camp Prong	Sevier	1.34	Low pH/ high	Undetermined

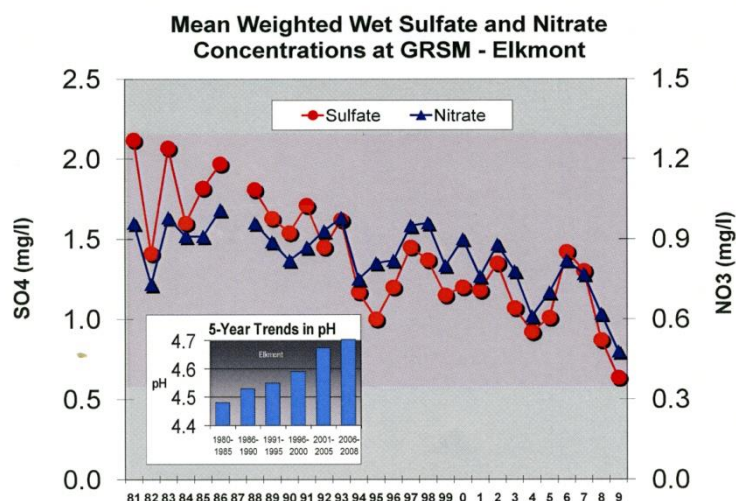


Figure 7. Changes in sulfate and nitrate deposition at the Elkmont monitoring station from 1981 to 2009 (from NPS, 2010).

The atmospheric deposition of both sulfate and nitrate has decreased within the Park since the early 1980s (Figure 7). On a park-wide basis, Robinson et al. (2008) used a multiple regression approach to determine whether pH and ANC as well as sulfate and nitrate concentrations in stream waters accompanied these known decreases in atmospheric acidic deposition. Regression models were based on data collected between October, 1993 and November, 2002 at 90 stream sites dispersed throughout the GRSM. The analysis revealed that pH decreased by 0.016 pH units per year over the monitored period. The regression model also demonstrated that pH was

strongly dependent on elevation, decreasing by -0.72 units per 1,000 m of elevation increase. Thus, improvements in stream water acidification did not appear to accompany declines in atmospheric acid deposition (Robinson et al., 2008). In contrast to pH, regression models created for ANC, nitrate and sulfate were found to exhibit no systematic change over the monitoring period when data from all of the monitoring sites were used.

Robinson et al. (2008) also examined temporal trends in acid-base chemistry from a suite of elevation classes. They found that pH declined at a rate of -0.0127 to -0.0260 pH units/yr at lower elevations, but showed little change through time at higher elevations (>3500 ft). Sulfate concentrations also decreased over the monitoring period at lower elevation sites. In contrast, no trends were observed for nitrate, whereas temporal trends in ANC values were mixed between the various elevation classes. However, where a statistical trend in ANC occurred, ANC values were declining, indicating that there was no improvement in stream water acidification (Robinson et al., 2008).

In addition to characterizing past trends in stream water chemistry, Robinson et al. (2008) developed regression based, forecasting models to assess future changes in water quality. They found that if the observed trends continue into the future, 30 % of the sampling sites will reach a pH of <6 (the reference threshold for biological effects) within 10 years; 63.3 % will acquire values <6 in 25 years and 96.7 % in less than 50 years.

An analysis conducted by Cai et al. (2012a) are, in general, consistent with the results provided by Robinson et al. (2008), although some minor differences exist as a result of differing approaches. Cai et al. (2012a) found that 67 of 92 sites with data from 1993-2009 exhibited no discernible trend in pH, whereas 22 sites improved from 0.01 to 0.03 pH units per year; 2 sites exhibited a decrease in pH of 0.03 units per year. Sulfate and nitrate concentrations showed no consistent trends when data were analyzed from all 92 sites collected between 1993 and 2009; both increases and decreases in annual concentration were observed.

With regards to base cations, data provided by Cai et al. (2010) suggests that Ca^{2+} , Mg^{2+} , and Na^+ were exported over the longer term. In contrast, 71 % of K^+ was retained, probably as a result of annual assimilation into forest biomass. These data are consistent with the observation provided by Cai et al. (2012b) that mean base cation saturation within the watershed soils equaled or were below 7 % of the CEC_e , and appears to have decreased from 9 % observed in earlier studies by Johnson and Lindberg (1992). These data suggest that prolonged acidic deposition has resulted in loss of base cations from the watershed, a phenomenon that could lead to long-term cation depletion from the soils and hinder the recovery potential of stream waters (Cai et al., 2010, 2012b).

The noted discrepancy between declining acid deposition with the GRSM and observed temporal trends in the concentrations sulfate and nitrate within stream waters suggest that sulfate and nitrate export is closely regulated by soil biogeochemical processes (Cai et al., 2012b). An understanding of these processes provides important insights into current and future trends in stream water acidification.

Within the Nolan Divide Watershed, Cai et al. (2012b) found that sulfate was observed to move quickly through the watershed during precipitation events, adding to stream acidification, but over the long-term 61 % of the sulfate was retained. Thus, the soils act as a sink for sulfate, and have yet to develop a steady-state condition with respect to atmospheric sulfate deposition. This is an important conclusion because it suggests that a future change in soil water concentration, related to a decrease in sulfate deposition, may lead to desorption. Desorption, in turn, may allow for the introduction of sulfate to stream channels, reducing the rate of water quality recovery (Cai et al., 2012b).

With respect to nitrogen, net nitrate export was observed within the Nolan Divide Watershed, indicating that biogeochemical processes related to nitrogen were important in regulating stream acidification. Surface soil horizons exhibited much higher concentrations of organic and inorganic nitrogen as well as base cations and Al than lower horizons. Organic nitrogen content of the surface horizons was particularly high. These high levels of organic nitrogen, combined with high nitrogen transformation rates, suggest that nitrate export to stream channels is biologically controlled by such processes as forest uptake, microbial mineralization and nitrification. These processes vary seasonally as they are depend on precipitation, soil moisture, and temperature. Thus, nitrate export tends to be enhanced during the winter months (Cai et al., 2010). More importantly, the data imply that a reduction in atmospheric nitrogen deposition might not directly and immediately affect nitrogen loss to stream waters. Rather, watershed characteristics (e.g., elevation and forest type) that influence microbial activity will have a significant influence on nitrogen export to streams (Cai et al., 2012b). In addition, the data support biogeochemical cycling models that suggest the recovery of watersheds from acidic deposition may take several decades to occur (Cai et al., 2011).

In light of the observed temporal trends in acid-base chemistry of the stream waters and the potential controls exerted on sulfate and nitrate export by surface soils, it appears that significant improvements in water quality with regards to acidification are unlikely in the near future in spite of the decrease in the region's acid deposition. Therefore, while variations in temporal trends are likely to exist, particularly between basins at different elevation, the overall condition of stream water acidification appears stable.

4.3.7.2 Dissolved Aluminum

Due to the potential toxicity of dissolved aluminum (Al) in acidic waters, a number of investigations have examined the concentration of dissolved Al within the GRSM, and its potential effects on aquatic biota (Huckabee et al., 1975; Deyton et al., 2009; Neff et al., 2009; 2012; Cai et al., 2012a). On a park-wide basis, Cai et al. (2012a) found that mean dissolved Al concentrations for both base flow and storm flow were below the 0.2 mg/L reference value utilized herein (Table 9). However, dissolved Al locally and episodically reached values in excess of 0.4 mg/L at monitoring sites within the Park, well above 0.2 mg/L level often cited as a potential criterion for biological effects. In addition, Cai et al. (2012a) argued on the basis of fish distributions within the Park that dissolved Al should be no greater than 0.08-0.09 mg/L for adult brook trout and 0.13 mg/L for rainbow trout.

Table 9. Summary to acid-base water chemistry collected at 387 sites within the GRSM from 1993 to 2009 for Al, and 2003-2009 for the remaining metals. (from Cai et al., 2012a).

Flow	Statistic	Al (mg/L)	Cu (mg/L)	Fe (mg/L)	Mn (mg/L)	Zn (mg/L)
Baseflow	<i>Median</i>	0.04	0.00	0.02	0.00	0.01
	<i>Mean</i>	0.06	0.01	0.02	0.01	0.02
	<i>Std</i>	0.06	0.01	0.03	0.03	0.03
	<i>Minimum</i>	0.01	0.00	0.00	0.00	0.00
	<i>Maximum</i>	0.45	0.11	0.23	0.26	0.16
Stormflow	<i>Median</i>	0.04	0.00	0.02	0.00	0.01
	<i>Mean</i>	0.06	0.00	0.02	0.01	0.02
	<i>Std</i>	0.06	0.01	0.02	0.05	0.03
	<i>Minimum</i>	0.00	0.00	0.00	0.00	0.00
	<i>Maximum</i>	0.41	0.08	0.10	0.38	0.16

Significant variability in dissolved Al concentrations were observed both spatially within the Park and temporally at any given monitoring station. The observed variability in Al concentrations correlated strongly with pH and ANC, presumably because the solubility of Al increases with decreasing pH. Thus, higher dissolved Al concentrations are generally found within higher elevation watersheds that tend to be characterized by higher rates of acid deposition, and lower pH and ANC. Cai et al. (2012a), for example, demonstrated using stream sensitivity maps for the GRSM that the toxicological impacts of pH, ANC, and dissolved Al primarily exceed toxicological thresholds along higher elevation streams (Figure 8, Cai et al., 2012a). However, they also noted that seven mid-elevation locations that should have trout were predicted on the basis of stream chemistry as no fish areas.

Temporally, higher dissolved Al concentrations were observed at a given site during stormflow events when pH and ANC episodically declined (Deyton et al., 2009; Neff et al., 2009, 2012)(Fig. 3, Neff et al., 2009). The magnitude of the change in Al concentration during an event can be significant; data collected between March, 2006 and May, 2007 at three monitoring sites within the Little Pigeon River watershed in the GRSM showed that Al concentrations increased by approximately 0.1 mg/L during storm events (Deyton et al., 2009). Thus, trout could be episodically subjected to toxic levels of dissolved Al.

Neff et al. (2009) demonstrated that whole-body sodium concentrations correlated with decreasing pH and increasing dissolved Al concentrations, and that whole body sodium losses (varying from 10-19 %) reached values consistent with physiological stress in native brook trout in low pH waters (<5.1) containing elevated Al concentrations (>0.2 mg/L). In addition, YOY brook and rainbow trout populations were found to be inversely correlated with dissolved Al concentrations, but not adults. It is possible, then, that YOY trout are more vulnerable than adults to the toxicological effects of dissolved Al.

Biological effects associated with elevated dissolved Al concentrations may also be related to the exposure of the Anakeesta formation, enriched in sulfide minerals, within the Park. Huckabee et al. (1975) attributed a kill of native brook trout and salamanders along a reach of Beech Flats

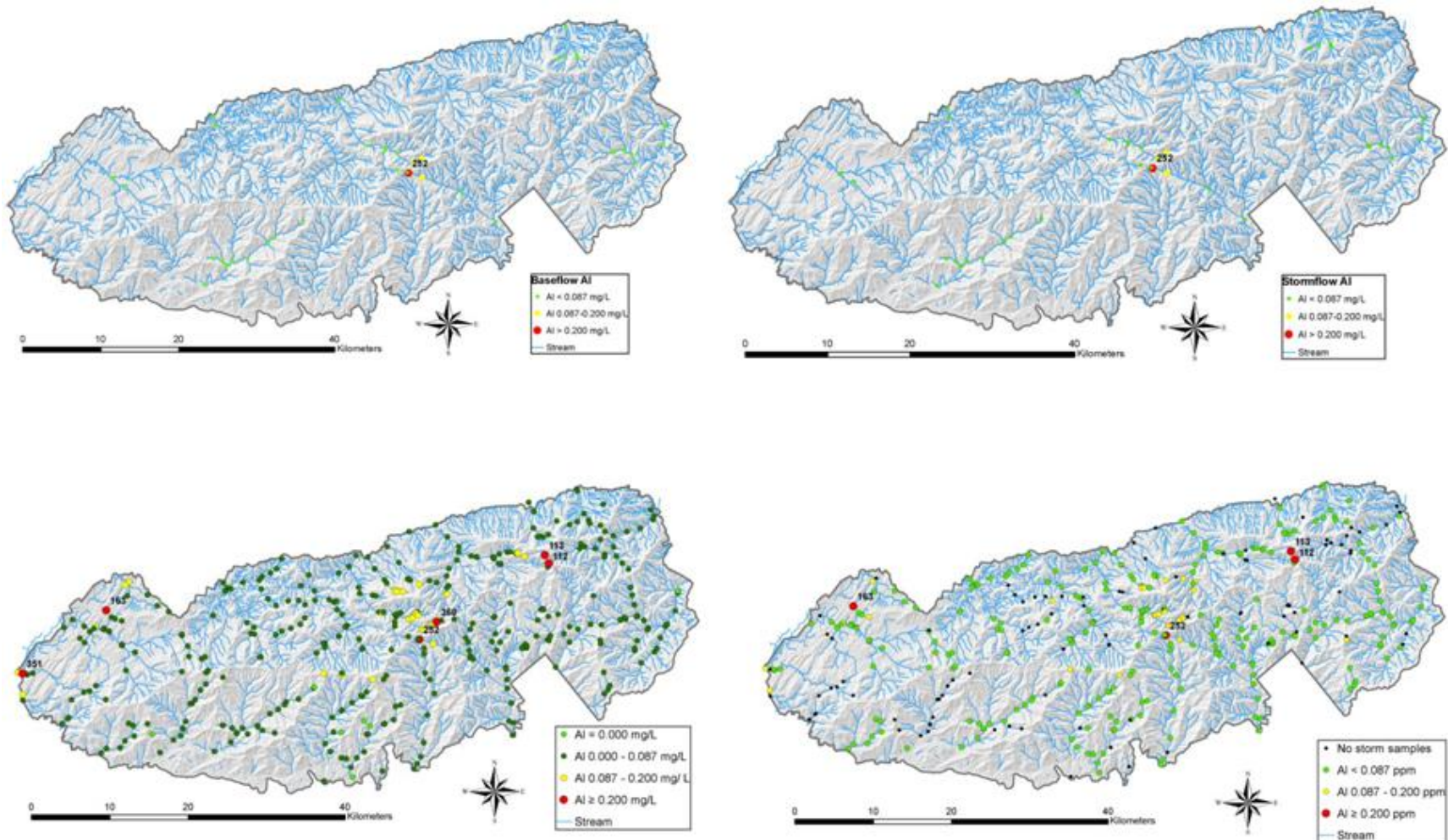
Creek to low pH waters (varying from 4.5-5.9) characterized by high Al (and Zn) concentrations. The observed pH and Al concentrations appear to have resulted from the influx of material associated with the construction of a road across the stream valley. Oxidation of the sulfide minerals within the road fill composed of the Anakeesta, and the subsequent leaching of the fill apparently led to a significant decline in stream water pH in comparison to upstream areas, and an increase in sulfate, Al, and Zn.

In light of the strong correlation between Al, pH, and ANC, and the potential effects of the observed water chemistry on trout and aquatic biota, it appears that Al is currently a significant water quality concern within the Park. In terms of its long-term temporal trend, concentrations appear to be stable, and are unlikely to change until pH and ANC within the stream waters recover. Recovery is likely to vary from site to site as demonstrated by mixed results in terms of temporal trend data. For instance, the 2010 water quality report found that median 2010 Al concentrations were 18 % higher percent than the 1993-2009 site medians on a park-wide basis, potentially indicating that dissolved Al values have increased slightly over time. However, Cai et al. (2012a) found that changes in annual dissolved Al concentrations over time varied from sited to site. At 67 of the 92 sites, dissolved Al concentrations exhibited no statistical change between 1993 and 2009. Ten sites exhibited decreasing annual dissolved concentrations over the same time period (in the range of 0.005 to 0.51 mg/L), whereas only 1 site exhibited an increase in dissolved Al concentrations over the monitoring period.

4.3.7.3 Other Metals

Data concerning the dissolved concentrations of trace metals in stream waters within the Park are primarily limited to Cu, Fe, Mn, and Zn. The concentrations of these elements measured at sites collected across all 387 sites between 2003 and 2009 (Table 9) are generally below the threshold toxicity criteria cited in Table 6 (Deyton et al., 2009; Cai et al., 2012a). Data collected between 2003 and 2008 were also examined for the 43 sites that are currently monitored. These sites (located within 7 watersheds) are thought to provide the data necessary to characterize the current condition of stream waters within the GRSM and to detect trends in stream water conditions through time (Odom, 2003). Metal concentrations for these sites are also low and are below the toxicity thresholds (reference values)(Tables 10). In fact, the majority of the Cu and Zn values were below the detection limit, whereas more than 40 % of the samples were below the detection limit for Fe and Mn.

Figure 8. Sensitivity maps shown the median aluminum concentrations during base flow (left) and storm flow (right) conditions for the 43 currently monitored stream survey sites (upper) and the 387 historical sites (lower) in the GRSM. Data were collected between 1993-2009. Aluminum concentrations are presented in mg/L and are estimates computed by a multiple regression model using $[H^+]$ and $[SO_4^{2-}]$ as predictors (from Cai et al., 2012a).



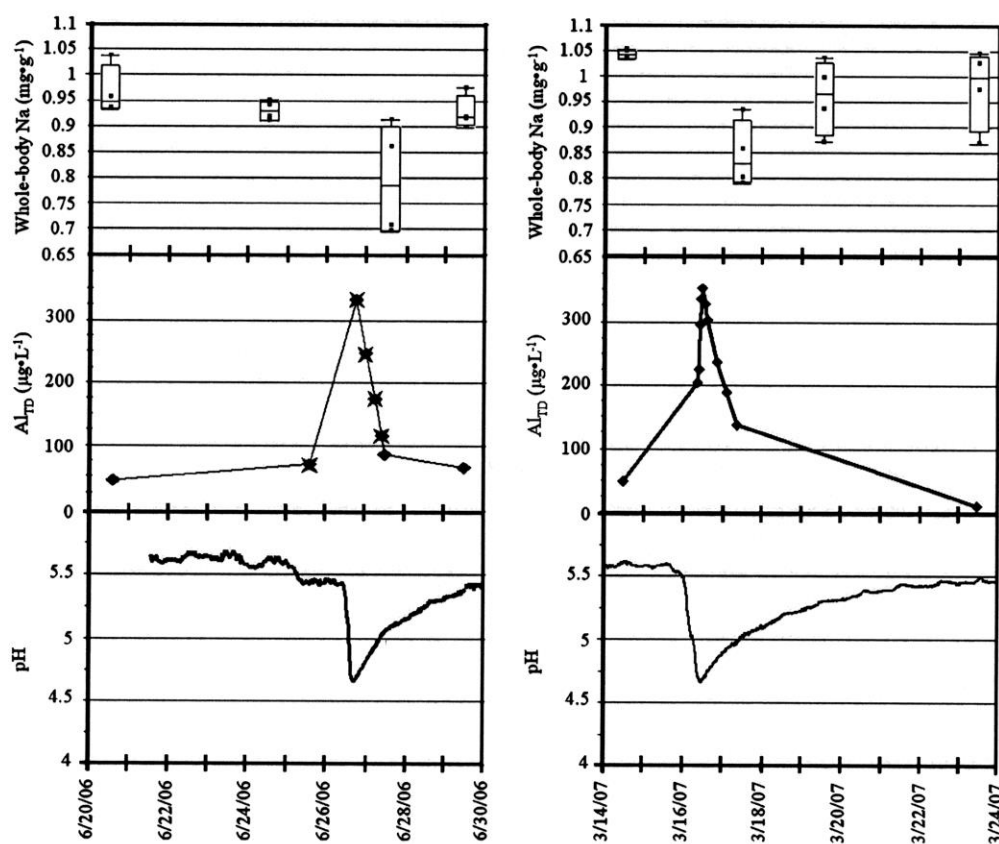


Figure 9. Typical relationships observed between whole-body sodium, total dissolved aluminum, and pH within studies sites within the GRSM. Data collected during runoff events in June 2006 and March 2007 at the Eagle rocks Prong Site (data and figure from Neff et al., 2009).

Table 10. Descriptive statistics for metal data collected at 43 sites monitored between 2003 and 2008.

Statistic	Cu	Fe	Mn	Zn
Median	0.030	0.028	0.144	0.018
Mean	0.038	0.086	0.483	0.142
Standard deviation	0.038	0.962	0.827	2.28
Minimum	0.012	0.002	0.002	0.008
Maximum	0.344	23.3*	4.40	51.71*
% Non-Detects	82.4	43.3	47.4	57.8
*Extreme outlier removed from data				

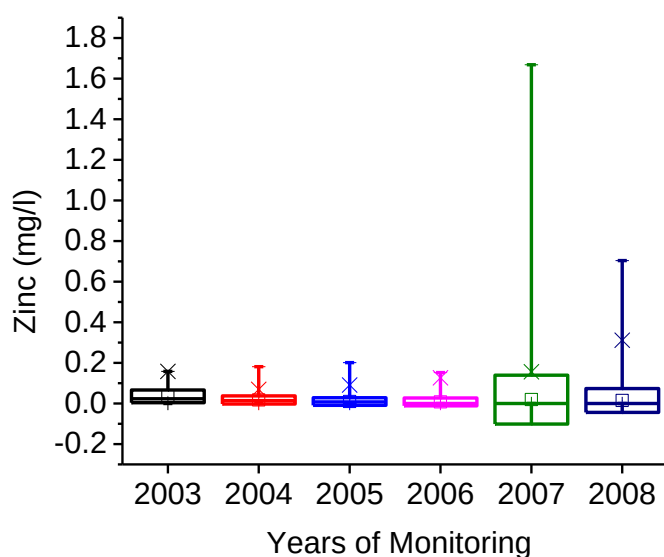


Figure 10. Zinc concentrations in the Great Smokey Mountain National Park. Data from 43 surface water quality monitoring sites and arranged by year. An outlier (51.71 mg/L) was removed from the 2008 data. - one standard deviation; whiskers - maximum and minimum values; small square – mean; x's are the 1%

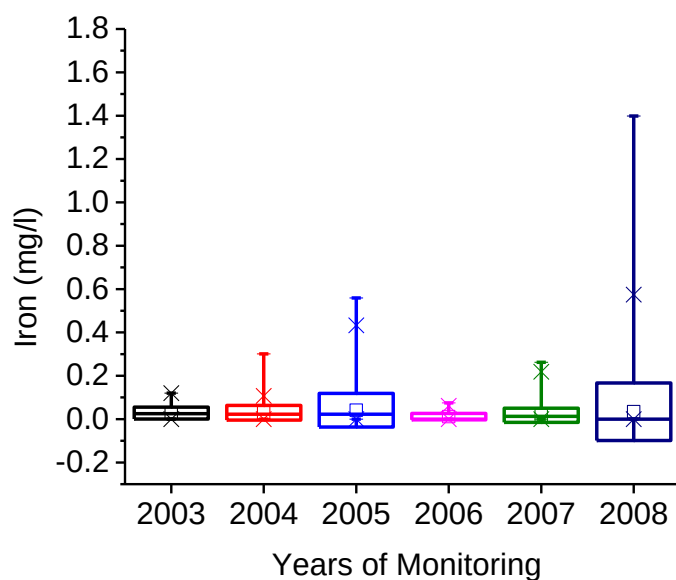


Figure 11. Iron concentrations in the Great Smokey Mountain National Park. Data from 43 surface water quality monitoring sites and arranged by year. An outlier (23.37 mg/L) was removed from the 2008 data. - one standard deviation; whiskers - maximum and minimum values; small square – mean; x's are the 1% and 99%; line in the box –median.

Analyses of Cu, Fe, Mn, or Zn concentrations reveal no significant trends in the data between 2003 and 2009. However, Figures 10 and 11 show that there was a significant increase in the range and maximum concentration of Fe and Zn in 2007 and 2008 when data from all 43 sites are considered. There is currently insufficient data available to determine if these values represent a longer-term trend or a statistical anomaly.

Additional trace metal data were summarized in the 1995 baseline water quality data inventory and analysis project within the GRSM (NPS, 1995)(Table 11). The data set includes monitoring sites both within and immediately adjacent to the Park. While the data show that drinking water

and/or freshwater criteria were occasionally exceeded, no particular element was observed to consistently exceed threshold values. Trace metal concentrations often increase during flood events. It is possible that the occasional measurements that exceed the criteria were collected during floods. However, the existing data do not allow for an assessment of the changes in metal concentrations during flood events.

Water quality data do not exist for a number of elements that are often associated with sulfide minerals and that therefore may be of importance (e.g., As, Cd, Cr, Ni, Pb, and Hg). Thus, while water quality with regards to the metals listed in Tables 10 and 11 appears to be good, there is insufficient data available at the present time to determine the current condition for a variety of toxic trace metals within stream waters on a park-wide basis or the potential trends through time in the metal data.

Table 11. Summary of water quality criteria compiled during the baseline water quality data inventory and analysis project within the GRSM (NPS, 1995).

Parameter	Period of Monitoring	# of Observation (# Stations)	Drinking Water Standard		Freshwater Criterion	
			Standard (µg/L)	# Exceeded	Standard (µg/L)	# Exceeded
Arsenic (As)	1970-1994	636 (31)	50	41	---	---
Cadmium (Cd)	1968-1994	374 (44)	5.0	7	3.9	9
Copper (Cu)	1967-1994	660 (72)	1,300	5	18	100
Chromium (Cr)	1967-1994	687 (47)	100	2	---	---
Iron (Fe)	---	---	---	---	---	---
Lead (Pb)	1967-1994	731 (45)	5	97	82	19
Manganese (Mn)	---	---	---	---	---	---
Mercury* (Hg)	1970-1994	691 (66)	2	6	2.4	6
Nickel (Ni)	1967-1994	461 (57)	100	13	---	---
Silver (Ag)	1968-1994	112 (25)	50	11	19	4.1
Zinc (Zn)	1967-1994	861 (74)	---	---	120	38

* Data quality suspect

4.3.7.4 Temperature

4.3.7.5 Specific Conductance

Data collected from 387 sites throughout the park between 1993 and 2009 exhibited mean specific conductance values of 14.52 and 15.93 $\mu\text{S}/\text{cm}$ for base flow and storm flow, respectively (Cai et al., 2012a). Specific conductance values are currently measured for 43 sites within seven watersheds throughout the Park. These sites are thought to provide the data necessary to characterize the current condition of stream waters within the GRSM and to detect trends in stream water conditions through time (Odom, 2003). Specific conductance was measured more than 2400 times between 1993 and 2008 at these sites; the mean value was determined to be 16.73 $\mu\text{S}/\text{cm}$. Less than 7 % of the measurements exceeded 50 $\mu\text{S}/\text{cm}$, the utilized reference criterion. On a site by site basis, only two sites, both on Abrams Creek, exceeded 50 $\mu\text{S}/\text{cm}$ (Table 12). The relatively high values along Abrams Creek can be attributed to the presence of carbonate bedrock within the watershed; thus, the values are not believed to denote a contaminant problem.

Figure 12 demonstrates that specific conductance has remained constant since 1993 for the currently monitored sites within the Park. On a site by site basis, regression analysis showed that while statistical significant changes in specific conductance occurred at 6 sites, the trends were extremely weak, exhibiting R^2 values of less than 0.1.

In light of the above, water quality is currently good with regards to specific conductance, and appears stable through time.

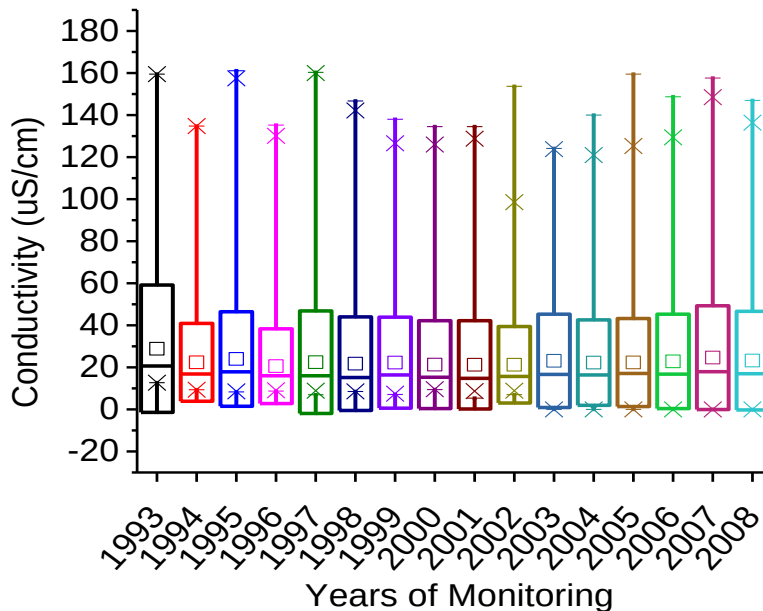


Figure 12. Specific conductivity measured at the 43 currently monitored sites within the GRSM between 1993 and 2008. Box - one standard deviation; whiskers - maximum and minimum values; small square - mean; x's are the 1% and 99%; line in the box - median.

Table 12. Descriptive statistics for specific conductance measured at the 43 currently monitored sites between 1993 and 2009. All measurements are listed in $\mu\text{S}/\text{cm}$.

Site							Standard
Site Name	Number	N	Median	Mean	Minimum	Maximum	Deviation
Lower Rock Creek	4	31	0.00	0.35	0.00	10.83	1.94
Little River at boundary	13	30	0.00	0.01	0.00	0.06	0.02
Lower West Prong Little R	24	74	22.25	22.78	7.01	35.10	5.13
W Pr Little Pigeon at headquarters	30	72	20.45	20.94	15.73	25.90	2.08
W Pr Little Pigeon at Chimneys Pic.	66	77	19.78	20.25	15.17	26.80	2.30
Road Prong above barrier cascade	71	73	15.82	15.98	5.36	23.00	2.04
Walker Camp Prong above Road Prong	73	75	20.90	21.16	15.60	26.90	2.55
Walker Camp Prong above Alum Cave Cr	74	74	25.00	25.38	16.17	35.10	3.88
Cosby Creek at log bridge	114	62	17.28	17.64	11.10	30.82	2.78
Upper Rock Creek (Cosby Creek)	137	73	14.90	15.06	10.00	20.30	1.91
Inadu Creek (Cosby Creek)	138	45	13.76	13.75	10.94	17.50	1.49
Beech Creek above Lost Bottom Creek	142	69	11.18	11.14	8.27	13.59	1.39
Lost Bottom Creek (Cataloochee Creek)	143	70	10.70	10.94	7.50	16.04	1.43
Palmer Creek above Pretty Hollow Cr	144	68	11.48	11.70	8.30	19.95	2.22
Lower Cataloochee Creek	147	71	14.80	14.72	10.50	18.60	1.77
Lower Little Cataloochee Creek	148	64	17.02	17.30	12.59	23.60	2.46
Mid Cataloochee Creek at bridge	149	63	14.54	14.66	11.00	20.30	1.69
Mill Creek above Abrams Creek	173	74	17.35	23.55	11.30	122.70	19.86
Abrams Creek below Cades Cove	174	72	106.55	102.62	0.71	161.10	43.13
Hazel Creek above cascades	221	37	10.70	10.65	6.32	16.30	1.82
Hazel Creek below Proctor Creek	224	8	11.30	10.86	6.56	12.42	1.88
Walker Camp Prong above Alum Cave	233	72	24.30	24.45	16.60	35.30	3.45
Upper Road Prong	234	60	16.04	15.70	9.90	17.88	1.45
Walker Camp Pr at last bridge	237	74	20.55	20.57	16.73	26.30	2.15

Site							Standard
Site Name	Number	N	Median	Mean	Minimum	Maximum	Deviation
Beech Flats above	251	71	31.60	30.26	9.33	40.30	6.92
Beech Flats below roadcut	252	71	49.80	45.86	15.38	76.40	14.94
Beech Flats above roadcut	253	72	24.50	26.28	17.93	94.81	10.62
Oconaluftee River below Smokemont	268	73	41.22	40.51	18.86	63.52	7.94
Beech Flats at Kephart footbridge	270	28	12.88	12.95	11.35	14.84	1.03
Rough Fork at Caldwell House	293	73	16.63	16.68	12.39	19.85	1.77
Bone Valley Creek (Hazel Creek)	310	42	12.57	12.81	6.72	19.00	2.31
Hazel Creek below Haw Gap Creek	311	41	11.80	11.98	6.64	17.50	1.86
Hazel Creek at campsite 86	479	37	11.84	11.90	6.64	18.50	2.12
Haw Gap Creek at bridge near campsite 84	480	37	13.50	13.55	6.75	19.00	2.26
Little Fork above Sugar Fork Trail	481	36	17.77	18.24	6.60	28.40	3.85
Sugar Fork above Little Fork	182	35	14.00	13.91	6.78	19.30	2.19
Sugar Fork above Haw Gap Creek	483	37	14.78	14.64	6.73	20.80	2.34
Hazel Creek at Cold Spring Gap Trail	484	36	10.66	10.87	6.60	16.90	1.64
Walker Creek above Hazel Creek Trail	485	35	11.26	11.38	6.68	14.44	1.66
Mill Creek at Pumphouse on Forge Cr Road	488	60	12.19	12.25	7.80	16.40	1.54
Abrams Creek 300 m below trailhead bridge	489	57	84.50	88.75	18.15	142.20	30.12
Camel Hump Creek off Low Gap Trail 2	492	59	16.57	17.02	11.57	23.40	2.16
Palmer Creek at Davidson Branch Trail	493	55	12.19	13.04	9.60	27.00	2.76

4.3.8 Data and Analytical Needs/Gaps

Three significant data needs have been identified that are critical to the evaluation of the current and future condition of water quality within the park. Each analytical/data gap is discussed below.

Reference Targets/TMDLs for nitrate and sulfate: Stream water acidification within the Park is primarily driven by high sulfate and nitrate concentrations, both of which vary spatially across the GRSM and temporally at any given site. The effective management of stream waters with regards to acidification will require an understanding of the maximum influx (loads) of sulfate and nitrate that will allow for the recovery of stream waters to acceptable pH conditions for the range of watersheds that exist. These maximum loads (potentially expressed as a total maximum daily load, TMDL) will likely require the development and use of rather sophisticated geobiochemical cycling models.

Additional Trace Metal Concentration Data within Stream Waters: Mercury (Hg) is considered a priority pollutant on a global scale, and is a pervasive contaminant of both aquatic and terrestrial ecosystems in the U.S. Once released into the environment, its biogeochemical cycling is highly complex, owing in part to the fact that it possesses a stable gaseous form, and may undergo a wide range of geochemical transformations, some of which are biologically mediated. The form predominantly accumulated in biota, for example, is methylmercury, a chemical species primarily produced by sulfate reducing bacteria. Once accumulated in biota, such as fish, it poses a risk to both ecosystem and human health.

Although numerous sources of Hg exist, atmospheric deposition serves as an important, if not the predominant, source of Hg to many terrestrial and aquatic ecosystems. It is emitted into the atmosphere from both natural sources (e.g., volcanic activity) and anthropogenic sources (e.g., fossil fuel combustion, precious metal mining, non-ferrous metal smelting, chlor-alkali plants, and waste incineration); 50 to 70 % of the atmospheric Hg is thought to be derived from anthropogenic sources. Coal-fired power plants are widely considered to be largest supplier of Hg to the atmosphere (EPA, 1997). Once in the atmosphere it can be transferred to terrestrial and aquatic ecosystems through wet and dry deposition, litter fall, throughfall, and cloud deposition (Fisher and Wolfe, 2012).

Data provided by the Mercury Deposition Network show that the GRSM is subjected to high rates of Hg deposition (Figure 13). In fact, Hg deposition rates are some of the highest recorded for national parks in the eastern U.S. (Figure 14)(NPS, 2010; Fisher and Wolfe, 2012). Although some data exist for stream waters, soils, sediment and biota within the park, the data are insufficient to effectively determine the current condition of surface waters in the Park with regards to Hg contamination.

Recent studies in the Southern Appalachians have also shown that a number of toxic trace metals and metalloids in addition to Cu and Zn may be derived from sulfide enriched layers within bedrock units which underlie the region (Miller and Mackin, 2013). The concentrations of these elements (e.g., As, Cd, Cu, and Ni) locally exceed threshold effect guidelines for aquatic biota in sediment and, during floods, stream waters. Although the limited existing data suggest that the concentration of these metals is typically low within the Park, it is important to recognize that an overwhelming majority of the data were collected during base flow conditions, or,

Figure 13. Map shown total wet mercury deposition in 2006 within the U.S. (from Mercury Deposition Network).

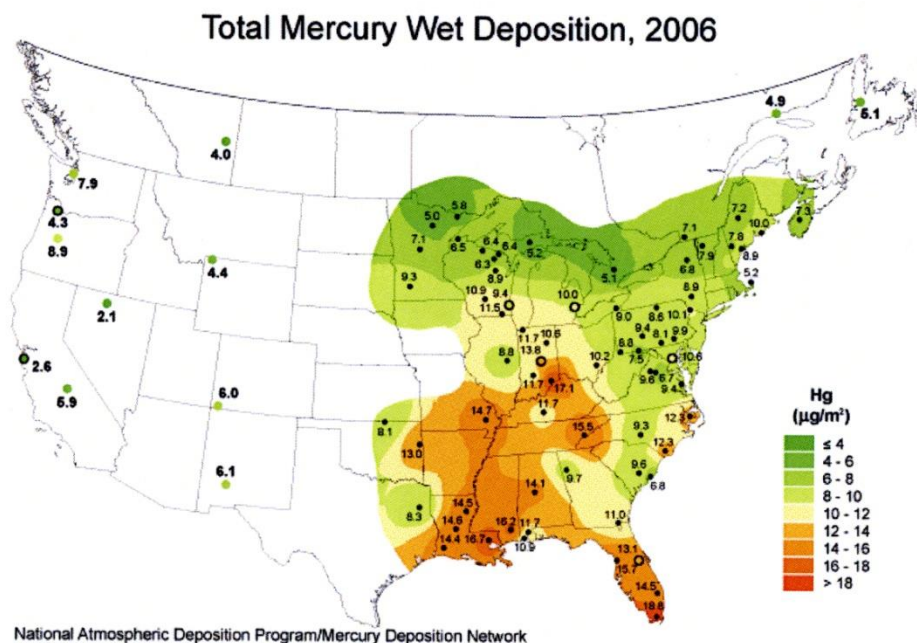
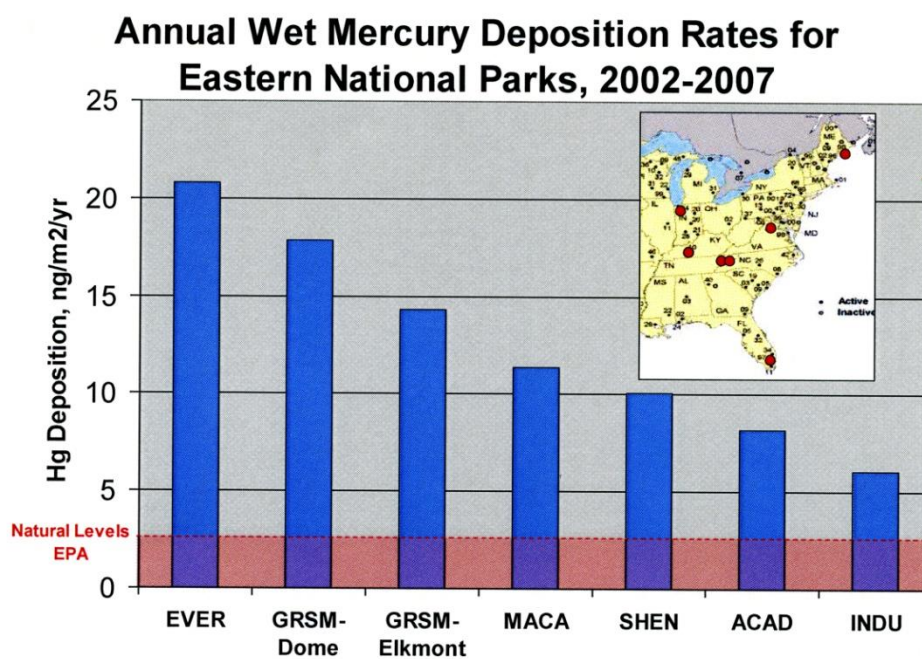


Figure 14. Comparison of annual wet mercury deposition rates measured in selected National Parks in the eastern U.S. between 2002 and 2007 (from NPS, 2010).



presumably, during the waning (falling) stages of a flood event, rather than during rising or peak stages when concentrations would be expected to be high. Data, then, are needed for additional metals collected over a wider range of flow conditions.

Inactive copper mines are located within two drainage basins within the Park: Eagle Creek and Hazel Creek. Both mines operated between approximately 1926 and 1944 and were closed when access roads to the mines were flooded by the closure of Fontana Dam. Visual observations suggest that acid mine drainage from the mines may be of concern (Thornberry-Ehrlich, 2008). For example, Sugar Fork, a tributary to Hazel Creek, drains tailings from the Hazel Creek mine, and mine tailings are visible along the channel. In addition, observations in 1992 and 2000 noted a lack of vegetation and aquatic biota for about 1 km downstream of the mines (Thornberry-Ehrlich, 2008), and dissolved Cu concentrations along the axial channel of Hazel Creek (including Sugar Creek) are statistically different from ($p < 0.05$) and higher than Cu measured at the remaining sites currently monitored within the Park. Drainage from the Eagle Creek Mine to Eagle Creek is via an ephemeral channel, and the effects are less visible. Nonetheless, additional trace metal concentration data are needed for both drainages (NPS, 2010).

Discharge/Flow Data: The concentration of many contaminants, including trace metals and the predominant anions driving stream water acidification, vary as a function of stream flow (Miller and Orbock Miller, 2007; Neff et al., 2012). Moreover, contaminant load calculations require discharge (stream flow) data. At the present time, discharge data are collected on a semi-continuous basis at two sites located within the Nolan Divide Watershed. However, flow data are generally lacking for most other monitoring sites located within the Park. Thus, only general relationships, typically based on local precipitation records, can be assessed between discharge and contaminant concentrations. The collection of discharge/water level data at additional sites throughout the Park is therefore needed to enhance the analysis and interpretation of water quality data on a park-wide basis.

4.3.9 Sources of Expertise

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