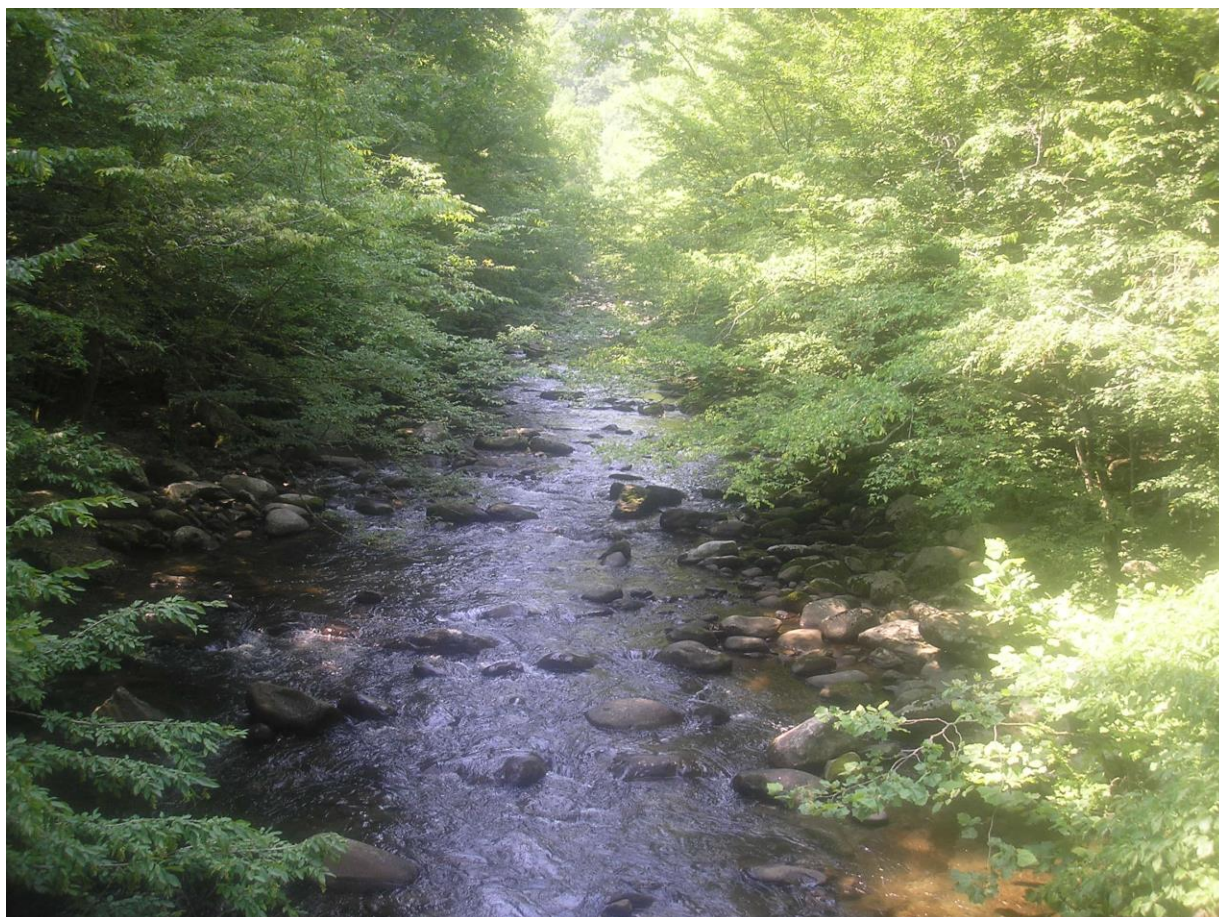




Biological Effects of Stream Water Quality on Aquatic Macroinvertebrates and Fish Communities within Great Smoky Mountains National Park

Natural Resource Report NPS/GRSM/NRR—2014/778



ON THE COVER

The Middle Prong of the Little River looking upstream of Tremont Institute bridge.
Photograph by: JS Schwartz, University of Tennessee, Knoxville, September 2006.

Biological Effects of Stream Water Quality on Aquatic Macroinvertebrates and Fish Communities within Great Smoky Mountains National Park

Natural Resource Report NPS/GRSM/NRR—2014/778

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Executive Summary

In the 1980s, the potential impact of stream acidification on aquatic ecosystems in Great Smoky Mountains National Park (GRSM) was a growing concern among park managers. Stream acidification is primarily caused by airborne acid pollutants generated from coal-burning power plants and vehicular traffic. Acids consisting of sulfate and nitric oxides, which are in greater amounts at higher elevations, are washed to the streams during rainfall events. Sampling and analysis of stream water during the 1980s found that pH and acid neutralizing capacity (ANC) dropped strikingly during stormflows to levels that were known to be lethal to trout. Concerned over the potential effects of acid deposition on water quality and aquatic biota, resource managers initiated a long-term monitoring program in the 1990s. Water quality sampling in GRSM streams began in 1993 with 357 stream sites monitored through 1995. The number and frequency of monitored stream sites for water quality changed over the years to the present program with 43 sites. Between 1990 and 2009, a total of 298 stream sites were surveyed for fish abundance, biomass, and habitat; and between 1990 and 2003, a total of 118 stream sites were surveyed for benthic macroinvertebrate richness, abundance, and quality metrics. The objective of this study was to statistically analyze this legacy water quality, fish, and benthic macroinvertebrate data in order to investigate the effects of stream acidification on aquatic biological communities, which can also guide development of future monitoring efforts to determine ecosystem health in GRSM.

Numerous statistical analyses were conducted with the three datasets for water quality (stream chemistry), fish (trout), and macroinvertebrates. These analyses included: 1) a temporal trend analysis investigating whether or not conditions are changing over time, 2) a spatial analysis examining what watershed characteristics influence stream chemistry and the distribution and abundance of biota, and 3) a biological impairment analysis examining relationships among watershed characteristics, stream chemistry, and biotic metrics. Before statistics could be applied, a major effort was undertaken to compile existing data into workable spreadsheets, and spatially collocate stream survey sites among the three datasets using GIS analysis. Seventy-five sites were found to be collocated among the three datasets, and 23 sites were collocated for all three dataset groups combined. Preparatory analyses with the water quality data also included the following: a classification of whether a sample was collected during baseflow or stormflow stage; an estimation of dissolved aluminum for years without metals analytical data; and an estimation of inorganic monomeric aluminum, a known toxin to trout, by use of a chemical equilibrium model and dissolved aluminum measurements.

The study also consisted of an extensive literature review to identify key chemical toxicological thresholds associated with stream acidification in order to support statistical analyses and interpret results. Stream pH toxicity levels have been classified into the following ranges: 1) pH 6.4 to 5.5 = slight impairment, 2) pH 5.5 to 5.0 = moderate impairment, 3) pH 5.0 to 4.0 = severe impairment, and 4) < 4.0 = lethal. Within the park-wide dataset for water quality (1993-2009), measured stream pH ranged from non-impaired to severely-impaired for both baseflow and stormflow conditions. About 13% of GRSM monitoring sites over the 16-year monitoring period were below the regulatory pH limit of 6.0, which provides a general idea of the extent of stream acidification across the park. State water quality standards for Tennessee and North Carolina require a pH in the range of 6.0 to 9.0. Within the current set of 43 sites sampled bimonthly, 10.8% of the samples for 2011 were below pH 6.0. Median total aluminum concentrations were

found to be below the toxicological threshold for both baseflow and stormflow conditions; however, during stormflows, this threshold has been exceeded. Although the literature reports an aluminum threshold of 0.2 mg L^{-1} , no adult brook trout were found in GRSM streams with aluminum levels above 0.09 mg L^{-1} , and adult rainbow trout were not found in streams with levels above 0.13 mg L^{-1} . These concentrations may reflect a more precise water quality threshold target specifically for GRSM streams.

Statistical evidence suggests that aquatic biota in GRSM's streams have been impacted by acidification. Maximum densities (fish per 100 m^2) for young-of-the-year (YOY) and adult brook and rainbow trout occurred when pH was above 6.0, and optimal densities occurred when pH was above 6.5. No brook or rainbow trout were collected in streams with pH lower than 5.5 and 5.8, respectively. Brook trout recruitment may be affected by chronic acidity, and overall, more study is needed to consider toxicological responses by YOY trout and episodic events, defined in terms of magnitude-duration-frequency and ecological end-points other than acute trout mortality. Macroinvertebrate metrics were also statistically different in streams with a pH above and below 6.0. Although macroinvertebrate communities were not found to be impaired at stream pH levels slightly below 6.0, comparatively better biological integrity occurred when stream pH levels were above 6.0.

Locations of stream survey sites in GRSM that exceeded pH, ANC, and total aluminum toxicological thresholds, identified as biologically sensitive areas, occurred at higher elevations. Streams above approximately 4000 ft (1219 m) receive higher levels of acid deposition than below this elevation; therefore, it was not unexpected that these streams were significantly lower in pH, ANC, and base cation levels, and higher in nitrate levels. Sulfate did not show a significant elevation trend. Streams with severe acidification (pH below 5.0) were located above 4200 ft (1280 m) elevation, and stream sites with pH below 5.5 were located above 3500 ft (1067 m), except for two streams in the Cosby Creek watershed. Many watershed characteristics were examined in this study, including site elevation, which was the dominant attribute, and others such as average basin slope, basin drainage area, percent area of Anakeesta geology, soil hydraulic conductivity (how fast water moves through soil), and forest cover type. Because observed changes over time were unique to a site's watershed characteristics, it suggests that acid-impaired streams will recover from the effects of acid deposition at different rates depending on these characteristics. Overall, elevation is a dominant watershed characteristic that is significantly related to stream chemistry in GRSM.

Relationships between watershed characteristics and stream water quality indicate that the storage and release of sulfate, nitrate, and base cations is controlled by soil sorption processes, forest-soil cycling, and groundwater. These factors regulate sulfate at baseflow, as indicated by the observed constant stream concentrations along an elevation gradient. However, sulfate concentrations may be increasing annually at higher elevation sites which could indicate that desorption of long-term stored sulfate in the soil is being transported to streams. During stormflow events, sulfate strongly influences episodic stream acidification, whereas nitrate and base cations do not. Also, there was some general indication that exposed Anakeesta rock may contribute to stream sulfate during stormflow periods, but the level of contribution is watershed dependent. Nitrate from atmospheric deposition exceeds forest uptake in GRSM and is mobile through the soil to the streams. Once in the stream, periphyton, plants, and biofilm take up nitrate, and as waters flow downstream, nitrate concentrations reduce. Forest type and condition

may influence nitrate uptake, storage, and release back to the soil because of the strong correlation with multiple parameters of water quality. It is possible that recent increases in stream nitrate could be influenced by the wide-spread hemlock die-off, during which wood decay reintroduces organic nitrogen to the soil and the nitrogen is converted to nitrate by microbes. More targeted monitoring and analysis is needed to assess whether this is occurring. In addition to forest nitrogen cycling, another important forest soil cycling process in headwaters is the storage and release of base cations, typically potassium, sodium, and calcium. In general, GRSM soils appear to have sufficient base cations, which are controlled by rock/soil weathering rates and groundwater transport along an elevation gradient. Under these controls, lower elevation streams generally receive groundwater inputs that have been in longer contact with rock/soil, thereby accruing base cations

Relationships between watershed characteristics and aquatic biota were dominated by elevation, which was significantly correlated with trout species distribution and macroinvertebrate metrics. While there were some exceptions, allopatric populations of brook trout were generally found in the higher elevation streams, allopatric rainbow trout were in the lower elevation streams, and sympatric populations were found at mid-elevations. Generally, brook trout metrics improved with elevation gain, whereas rainbow trout and macroinvertebrate metrics generally decreased with elevation gain. Because of these elevation trends with biotic metrics, applied statistics with water quality parameters and biotic metrics were influenced by collinearity; however, because sulfate concentrations did not exhibit an elevation gradient, it was a useful parameter for analysis. Also, the use of collocated sites between water quality and allopatric trout populations reduced the influence of elevation collinearity.

Findings from this comprehensive data analysis provided valuable information on the relationships between watershed characteristics, water quality, and aquatic biota. Results documented the extent of the acidification impacts on aquatic biota, and identified that the most biologically sensitive areas generally occur at the higher elevations. Results will guide future site selections for GRSM's Vital Signs monitoring program, currently under development by the National Park Service resource management staff.

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List of Acronyms

Biota, Watershed, and Other

ACFI	abundance of collector-filterers
ADT	adult
ACGA	abundance of collector-gatherers
APRE	abundance of predators
ASCR	abundance of scrapers
ASHR	abundance of shredders
AT	Appalachian Trail
BIOC	bioclassification score
Biom	biomass
BKT	brook trout
COV	covariance coefficient
Den	density
df	degree of freedom
EPTR	EPT richness
EPTA	EPT abundance at the unit of %
GRSM	Great Smoky Mountains National Park
I&M	Inventory and Monitoring
IFS	Integrated Forest Study
Ksat	soil hydraulic conductivity
NADP	National Atmospheric Deposition Program
NC	North Carolina
NCBI	North Carolina Biotic Index
QA/QC	quality assurance/quality control
RBT	rainbow trout
RCFI	richness of collector-filterers
RCGA	richness of collector-gatherers
RPRE	richness of predators
RSCR	richness of scrapers
RSHR	richness of shredders
Std	standard deviation
TA	taxa abundance
TDEC	Tennessee Department of Environment and Conservation
TMDL	total maximum daily load
TOT	total
TR	taxa richness
YOY	young of the year

Chemical

ANC	acid neutralizing capacity
BCS	base cation surplus
Ca ²⁺	Calcium
Cl ⁻	Chloride
Cond	water conductance
DOC	dissolved organic carbon
K ⁺	Potassium
Mg ²⁺	Magnesium
Na ⁺	Sodium
NH ₄ ⁺	Ammonia
NO ₃ ⁻ ; or NO ₃	Nitrate
SO ₄ ²⁻ ; or SO ₄	Sulfate

1.0 Introduction

1.1 Overview: Water Quality Monitoring Program

In the 1980s, the potential impact of stream acidification on aquatic ecosystems in Great Smoky Mountains National Park (GRSM) was a growing concern of resource managers. This concern existed not only in GRSM, but throughout the eastern United States where excessive atmospheric acid pollutants are deposited on regions with base-poor bedrock (Herlihy et al. 1991, Hyer et al. 1995, Wigington et al. 1996a, 1996b). Major contributors of acid deposition are sulfate and nitrate acid anions generated from coal-burning power plants and vehicular traffic. Streams in base-poor geological regions lack the capacity to buffer acid rain inputs, becoming chronically acidified, and they can experience episodically pronounced short-term drops in pH and acid neutralizing capacity (ANC) during stormflows. Cook et al. (1994) first reported on episodic acidification in GRSM headwater streams from water samples collected in 1985, where they found that pH dropped one unit to 4.8 and ANC dropped to $-48 \mu\text{eq L}^{-1}$ during stormflow episodes. In addition, effects of acidic deposition on GRSM water quality were documented as part of the Integrated Forest Study (IFS), an American and European program to study acid rain effects on forest nutrient cycling (Johnson and Lindberg 1992, Lindberg and Lovett 1992). In GRSM, Noland Divide watershed was the IFS site, and after the study was completed in 1991, resource managers initiated a long-term monitoring program to specifically investigate the impacts of acid deposition on stream and soil water quality at the Noland Divide watershed.

Concurrently in the 1980s, environmental studies found fish and aquatic macroinvertebrates to be impaired from stream acidification (Driscoll et al. 1980, Gagen and Sharpe 1987, Weatherby and Ormerod 1987, Hurley et al. 1989, Ingersoll et al. 1990, Cleveland et al. 1992, Simonin et al. 1993, Kimmel et al. 1996). In the Appalachian region, there was major concern for the loss of native brook trout (*Salvelinus fontinalis*), where extirpation had been reported from severely impacted streams (Baker and Schofield 1982, Carline et al. 1992, Baker et al. 1996, Webb et al. 2004). The physiological mechanism of fish death, or sublethal stress to acid conditions, is ion regulation disturbance leading to circulatory collapse (Hunn 1985, Booth et al. 1988, Hermann et al. 1993). Increased acidity and concentrations of dissolved monomeric aluminum (Al_{M}) interfere with gill ion transport by replacing calcium on gill surfaces and also causing excessive whole body loss of sodium. Acid toxicity in brook trout causing asphyxia is reported to occur in the pH range of 5.5-6.4, and potential lethal effects occur in the range of 4.2-4.8 (Neville and Campbell 1988). In order to investigate the potential biological effects of acidic deposition in GRSM, resource managers implemented an Inventory and Monitoring (I&M) Program in 1993. In this long-term monitoring program, stream water quality, aquatic macroinvertebrate communities, and fish populations were identified as key early warning indicators of acidification in GRSM's aquatic ecosystems.

The specific goals of the initial I&M Program were to: 1) establish and implement a monitoring program to measure changes over time of key water quality parameters, aquatic macroinvertebrate communities, and fish populations or communities in representative aquatic systems; 2) analyze and present data to managers on assessment of biotic condition and provide practical information aiding in the protection and preservation of park natural resources; and 3) establish and implement a prototype monitoring program, which could be used to guide development of monitoring programs in other National Park Service units. Between 1993 and 1995, the water quality program, known as the *Park-wide Stream Survey*, consisted of the

collection of water samples at a total of 357 stream sites. This water quality monitoring program continues today, although the sampling frequency and site numbers have changed over time. Water quality data have been collected at a total of 387 sites through 2009. Fish population data have been collected at a total of 298 stream sites, and aquatic macroinvertebrates have been sampled at 118 stream sites. Fish and macroinvertebrates were monitored on an annual basis during summer months, where subsets of the total survey sites were monitored each year. Details on the stream sites and monitoring frequencies are described in the Methods section. Although individual indicator analyses have been conducted, an integrative analysis of water quality, fish, and aquatic macroinvertebrates has not been conducted with the I&M monitoring datasets to comprehensively quantify the biological effects of stream acidification.

1.2 Study Objective

The objective of this research study was to analyze legacy water quality, fish, and benthic macroinvertebrate data in order to identify potential effects of baseflow and stormflow chemistry on these aquatic biological communities. This study also included a comprehensive literature review of toxicological thresholds for fish and macroinvertebrates, and an assessment of GRSM water quality data identifying stream sites exceeding the thresholds. In this study, relationships between watershed basin characteristics and the water quality, fish, and macroinvertebrate monitoring data were investigated using the complete set of databases. GIS-based data for watershed characteristics were compiled, which included watershed basin area, average slope, channel density, site elevation, stream order, soil hydraulic conductivity, and percent land areas of soil, vegetation, and surficial geology classification types. Surficial geology specifically included the Anakeesta formation, which contains pyrite and when exposed to weather can release sulfuric acid. There was a focused effort to assess streams on the 303(d) list, in which baseflow pH is less than 6.0, and eight streams in the Neff (2010) study examining influences of watershed characteristics on water quality.

Effects of water quality on fish and macroinvertebrates were investigated by both temporal and spatial analyses. Statistical analyses of the final compiled water quality, fish, and benthic macroinvertebrate datasets included the following investigations: 1) a time trend analysis to define changes in stream chemistry and aquatic biotic metrics from 1993 to 2009; 2) a spatial characterization of stream chemistry and biotic metrics among the survey sites compared with watershed characteristics; and 3) an analysis correlating stream chemistry and biotic metrics to identify possible relationships with effects of stream acidification. Data compilation and database development, toxicological assessments, and statistical analyses are described in detail in the following sections. Overall, this study provides valuable management information to guide revisions to the I&M Program, in which development of an ecosystem health, indicator-focused vital signs monitoring program is currently in progress (GRSM 2010).

2.0 Database Development

2.1 Methods Overview

To meet the study research goals, I&M monitoring data for water quality (stream chemistry), fish, and benthic macroinvertebrates were analyzed using several statistical approaches. Before statistics could be applied, a major effort was required to compile the existing data into workable spreadsheets, assess data quality, and parameterize data (Section 2.2). GIS analysis was required to spatially determine where stream survey sites for the three monitoring indicator groups were collocated; that is, compile data so that water quality, fish, and macroinvertebrate sample sites that were geographically close enough could be analyzed as a common site (Section 2.2.4). In addition, sampling collection dates were compared to identify temporally correlated survey sites. Within each of the three monitoring indicator groups, relevant parameters (metrics) had to be selected for the statistical analysis; for example water quality included chemical parameters (pH, ANC, conductivity, SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , base cations, and dissolved metals) and fish included density, biomass, and the condition factor K. Analysis of fish species was limited to brook trout (*Salvelinus fontinalis*) and rainbow trout (*Oncorhynchus mykiss*).

Water quality datasheets developed for statistical analyses also needed to be organized in order to identify whether water samples represented baseflow or stormflow water chemistry (Section 2.3). Water samples were collected on regular schedules and not based on stream flow stage or time interval following precipitation events; therefore, an analysis was developed to delineate whether water samples were taken during baseflow or stormflow. This approach utilized rainfall data from several weather stations in or near GRSM, and it is described in detail below.

Another issue with the long-term water quality database was the lack of dissolved metals analysis prior to 2003 (Section 2.4.1). In particular, dissolved aluminum was not analyzed and this metal is an important chemical indicator of fish toxicity, particularly the monomeric aluminum (Al_{IM}) form. A geochemical equilibrium model was used to estimate what percentage of measured total dissolved aluminum would be in the Al_{IM} chemical form based on pH and other chemistries. In addition, a preliminary statistical analysis was conducted to develop a predictive relationship for dissolved aluminum based on other chemical parameters. Although, a statistical predictive model is only an estimate, it provides a means to examine the possible effects of dissolved aluminum on aquatic biota with the water quality data prior to 2003.

2.2 Sites and Parameters Description

As noted in the Introduction, GRSM water quality, fish, and benthic macroinvertebrate surveys began in 1993 with the initial I&M Program. Datasets analyzed for this study included 387 water quality (stream chemistry) sites, 298 fish survey sites, and 118 macroinvertebrate survey sites. Water quality and fish surveys continue to be conducted, but not for all sites. Details on the number of stream survey sites, collection frequencies, and periods of record are described below in Sections 2.2.1, 2.2.2, and 2.2.3. Site selection and sample timing for the most part were not coordinated among the three monitoring programs; therefore, an initial step in this study was to collocate stream sites spatially and temporally within concurrent periods. Methodology for this effort is described in Section 2.2.4.

2.2.1 Water Quality Survey Sites and Chemistry Monitored

Water quality monitoring began in 1993 with a total of 185 stream sites (Figs. 1, 2). In 1994, 119 sites were added to the stream survey and in 1995 an additional 53 sites were added. Between the years 1993 and 1995, the initial 185 stream sites were sampled on a semi-annual basis and the remaining 172 sites were sampled at different frequencies. In 1996, the number of sample sites was reduced to 160 collected on a monthly basis, and in 1997, the number of sample sites was reduced to 90 collected quarterly. In 2004, the number of samples sites became 32 collected bimonthly, and 11 Hazel Creek sites collected biannually. Among the 43 survey sites monitored since 2004, 27 have a complete monitoring history from 1993 through 2009. In total, during the period 1993 to 2009, 387 sites were monitored for stream chemistry at least once. Detailed tabulation of water quality survey sites and monitored periods per site is in Appendix 1.

Stream chemistry was analyzed for pH, gran ANC, conductivity, acid anions (Cl^- , SO_4^{2-} , NO_3^-), ammonia (NH_4^+), and base cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+). Beginning in 2003, dissolved metals (Al, Cu, Fe, Mn, Si, and Zn) were added to the chemical analysis. Because of the reduction in stream survey sites after 2003, only 43 sites have metal analysis data (Fig. 2). Between 1993 and 1997, laboratory analyses were conducted by staff in the University of Tennessee, Knoxville (UT) Department of Forestry, Fisheries and Wildlife. Beginning in 1998, analyses were conducted by staff and students in the UT Department of Civil and Environmental Engineering (CEE). The CEE Department used a ManTech™ autotitrator for pH, gran ANC, and conductivity. A Dionex™ ion chromatograph (IC) was used for the analysis of Cl^- , SO_4^{2-} , NO_3^- , and NH_4^+ . A Thermo-Scientific™ Inductively Coupled Plasma – Atomic Emission Spectrometer (ICP-AES) was used for the analysis of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Al, Cu, Fe, Mn, Si, and Zn. Quality assurance/quality control (QA/QC) procedures included blanks, replicates, spikes, and USGS round-robin checks. Annual QA/QC records are documented in annual reports for the water quality monitoring program, which for recent years can be retrieved from the US National Park Service database NPSTORET (http://www.epa.gov/storet/dw_home.html).

2.2.2 Fish Survey Sites and Trout Metrics

Annual fish surveys began in the 1980s and continue to present day. Between 1986 and 2009, a total of 298 fish survey sites have been monitored (Fig. 3), reporting 38 fish species. Because stream acidification occurs in GRSM at higher elevation areas where brook and rainbow trout occur, this study focused on these two species. Fish surveys were conducted using standard three pass-removal procedures with backpack electrofishing gear. At each survey site, stream wetted width (m) and length (m) were measured. Fish were identified by species and classified as young of the year (YOY) or adult based on fish length. In general, brook trout less than 90 mm in length were YOY, and greater than 95 mm were adult. For rainbow trout, YOY were less 100 mm and adults were greater than 115 mm. Total density and biomass were reported per survey site reach. In this study, trout metrics computed were:

- *Density* – Per species and size class, density was calculated by dividing the estimated number of fish by the surface area sampled (m^2), multiplied by 100 to convert the metric to units of *number of fish per 100 m²*.
- *Biomass* – Per species and size class, biomass was calculated multiplying the site average weight (g) by species/size class estimate, and dividing by the site survey surface area (m^2). The resulting unit (g/m^2) was then multiplied by 10 to convert the metric to units of *kg/ha*.

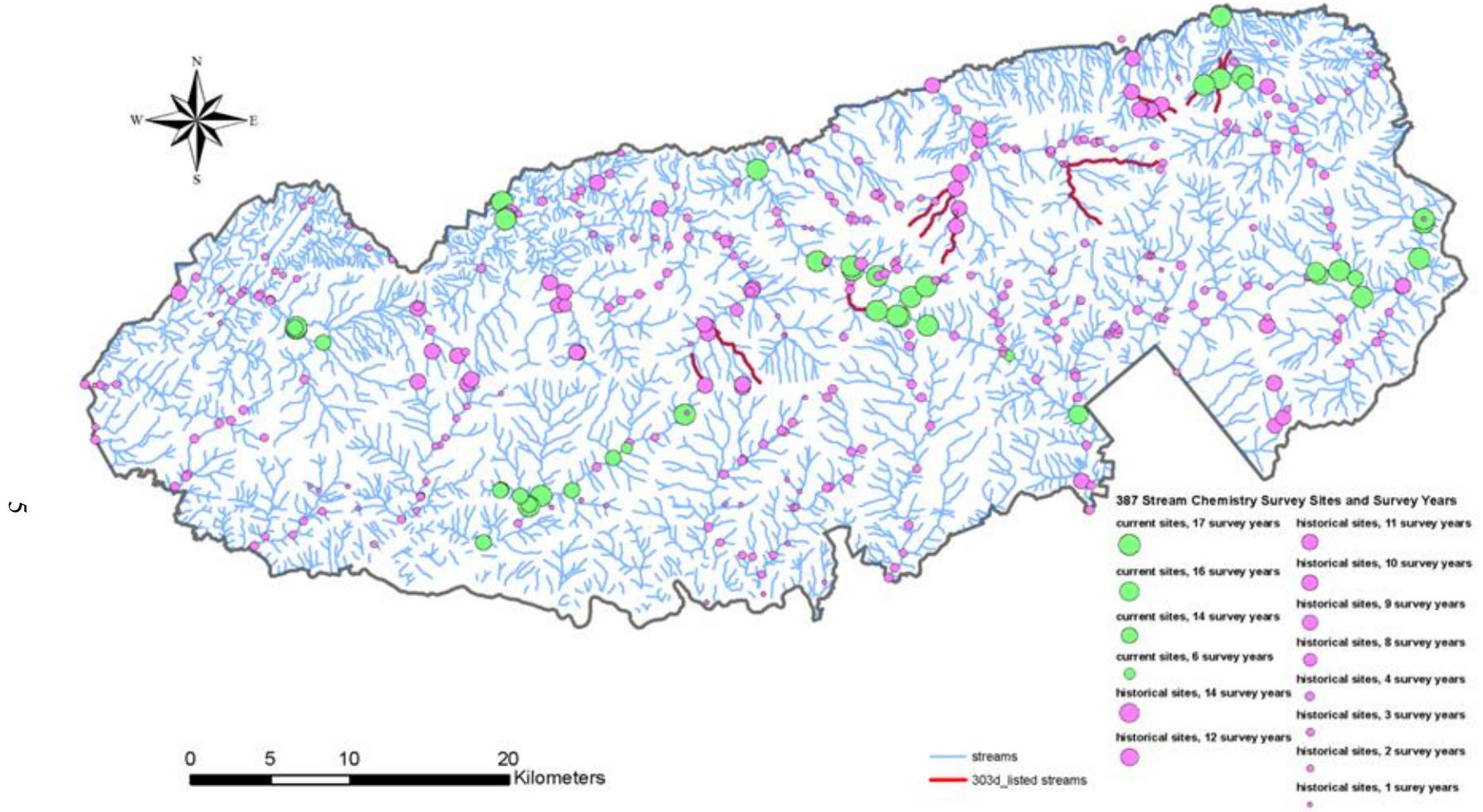


Figure 1. Water quality (stream chemistry) survey sites in Great Smoky Mountains National Park monitored for stream chemistry from 1993 to 2009. Survey sites are delineated per number of sample records. Streams on the 303(d) list are shown in red.

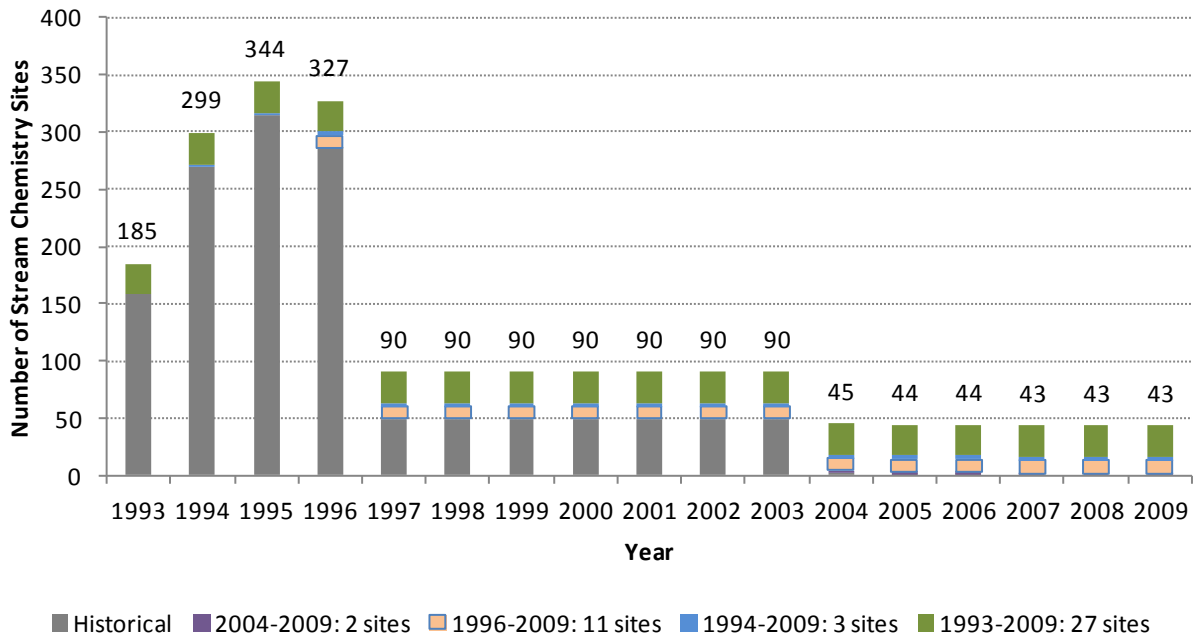


Figure 2. Water quality monitoring program: number of stream survey sites sampled per year from 1993 to 2009, including a continuous site count for the sampling period of record.

- *Condition factor K* – Condition factor, a measure of fish well-being, was computed by relating its weight (g) and length (mm). The mathematical equation to quantify the Fulton *condition factor (K)* is as follows:

$$K = \frac{10^5 W}{L^3}$$

where, W is fish weight in grams (g) and L is fish length in millimeters (mm).

In some cases, computed values for condition factor K generated some extreme estimates, for example 0 and 1600. Extremely low and high K values were considered unreasonable and were excluded from the study analyses. Criteria for extreme K values were set as less than 0.5 and greater than 2.25. This condition factor K range was based on the chart reported in Barnham and Baxter (1998).

In addition to site surveys for density and biomass, a salmonid (trout) distribution map was generated from fish surveys conducted between 1994 and 2000 (Fig. 3). In this specific effort, surveys were conducted using backpack electrofishing gear where field crews began at a downstream point on a river or stream and moved upstream noting trout absence or presence. Surveyors noted elevations as they proceeded upstream electrofishing, and any significant habitat features and possible barriers limiting upstream fish movement (i.e., waterfalls, cascades). Fish surveys continued until no trout were encountered, and all tributary streams within a watershed were surveyed. Physical and chemical stream parameters were measured at the upstream extent of a species distribution, routinely including: channel mean wetted width (m), dominant substrate type, barrier height (m), stream gradient (%), temperature (°C), and conductivity (µS/cm). In some cases, more extensive water quality measurements were taken. The trout distribution map

identifies reaches which were occupied by allopatric populations (single species), and sympatric (two or more species) populations.

Fish Survey Sites in the Great Smoky Mountains National Park

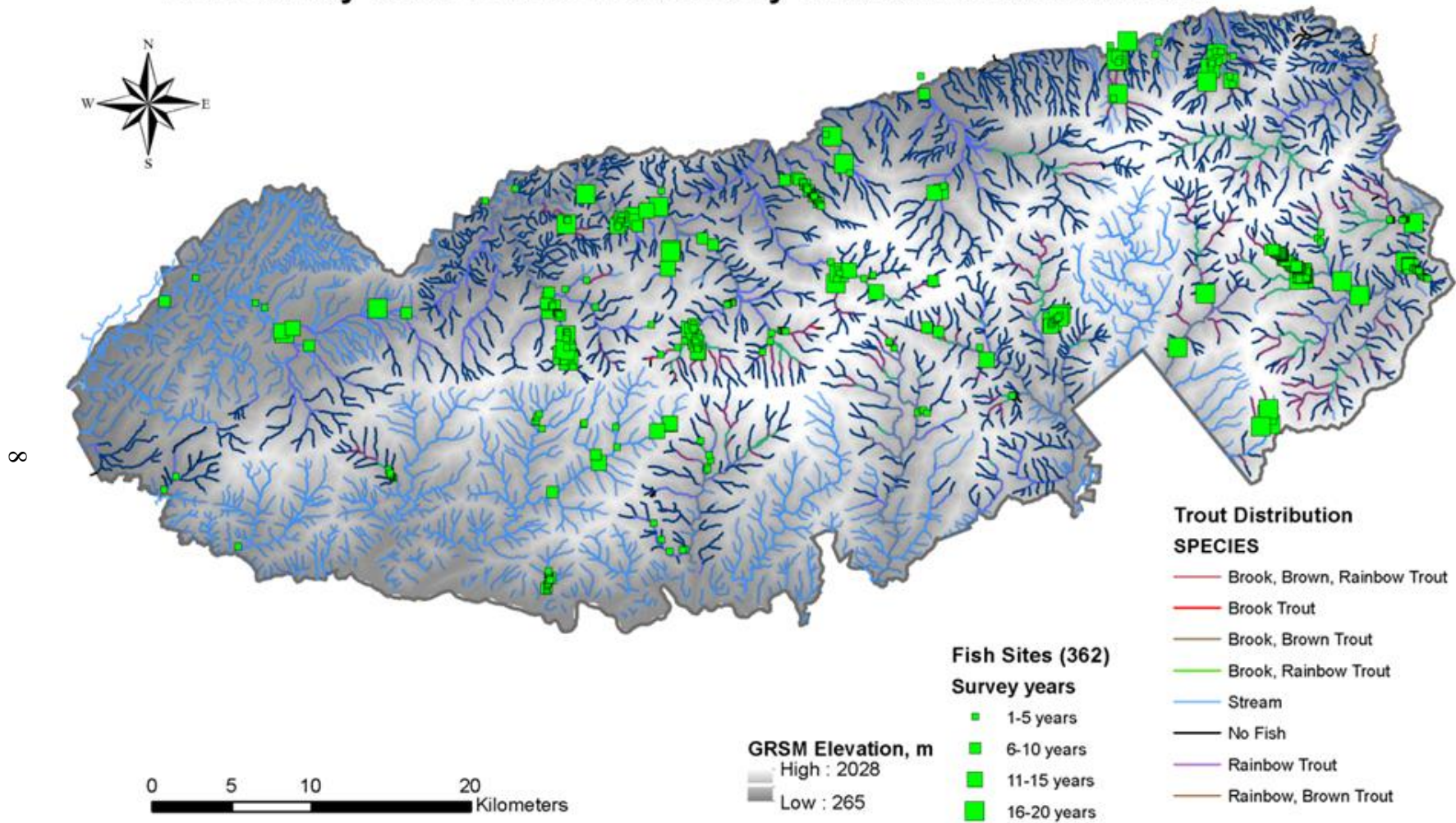


Figure 3. Fish survey sites and trout distribution in Great Smoky Mountains National Park. Fish surveys conducted from 1990 to 2009, and trout distribution based on sampling from 1994 to 2000.

2.2.3 Macroinvertebrates Survey Site and Biotic Metrics

A total of 118 sites were surveyed for benthic macroinvertebrates between 1990 and 2003 (Fig. 4). Annual collections were made from March to November, but primarily during summer months. It is noted that 82 of the 118 sites had only one year of data. Benthic macroinvertebrate collections were conducted within a 100-m reach using multiple devices including D-nets for sampling multiple habitats (i.e., root mats, undercut banks), kick nets for riffle habitats, sieve buckets for leaf pack sorting, and a sand net. Sampling also included a visual search of rocks and large immovable boulders and logs. As prescribed by NCDENR (2011), standard metrics for benthic macroinvertebrates that were computed and used in this study's analyses were as follows:

- *EPT Richness and Abundance.* EPT richness is the total number of species within the orders of Ephemeroptera, Plecoptera and Trichoptera, per site collection. Taxa that could only be identified to family are included only if they were the only taxon found in that family. EPT abundance is the total number of EPT individuals per site collection.
- *Taxa Richness and Abundance.* Taxa richness is the total number of distinct species found per site collection. Taxa abundance is the total number of individuals per site collection.
- *North Carolina Biotic Index (NCBI).* This index is computed by:

$$NCBI = \frac{\sum x_i t_i}{n}$$

where, x_i is the abundance code (1, 3, or 10) for each taxon, based on the number of specimens collected. One to two specimens are coded as 1; 3 to 9 specimens are coded as 3; and 10 or more specimens are coded as 10. Tolerance values (t_i) for the i^{th} taxon range from 0 for very intolerant species to 10 for very tolerant species; values can be obtained in NCDENR (2011); and n is the sum of all abundance codes.

- *Bioclassification Scores.* In most mountain streams of the southeastern US, equal weight is given to both EPT taxa richness and the NCBI when assigning bioclassification scores (Table 1). These scores correspond with the following stream quality ratings: 5 = Excellent; 4 = Good; 3 = Good-Fair; 2 = Fair; and 1 = Poor. For each site collection, bioclassification scores based on EPT taxa richness and the NCBI are then averaged and rounded to produce the final bioclassification score. If the two individual scores before averaging differ by one, resulting in a final score midway between the two scores, the total number of EPT individuals (EPT N) is used to determine whether to round up or round down. If EPT N is greater than the criteria listed below the final score is rounded up, and if it is less the final score is rounded down:

Excellent (5) vs. Good (4)	191
Good (4) vs. Good-Fair (3)	125
Good-Fair (3) vs. Fair (2)	85
Fair (2) vs. Poor (1)	45

- *Functional Feeding Group Richness and Abundance.* Functional feeding groups include: collector-filterer, collector-gatherer, predator, scraper, shredder, and unknown (Barbour et al. 1999). Per functional group, richness is the number of species per collection, and abundance is the number of individuals per site collection.

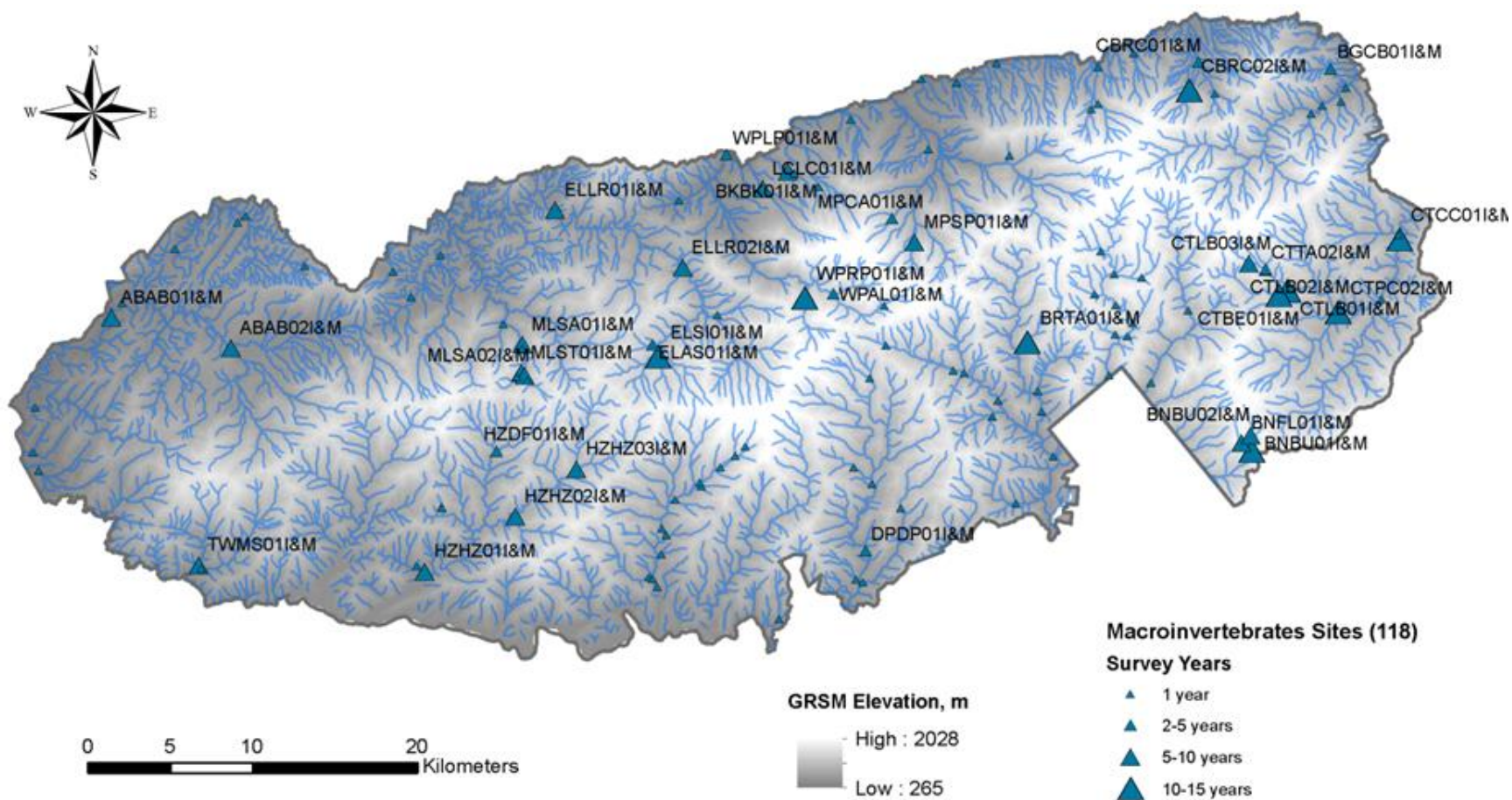


Figure 4. Benthic macroinvertebrate survey sites in Great Smoky Mountains National Park from 1990 to 2003.

Table 1. Criteria for bioclassification scores using EPT taxa richness and NCBI values.

Bioclassification Score	EPT Richness	NCBI
5.0	> 43	< 4.00
4.6	42 – 43	4.00 - 4.04
4.4	40 – 41	4.05 - 4.09
4.0	34 – 39	4.10 - 4.83
3.6	32 – 33	4.84 - 4.88
3.4	30 – 31	4.89 - 4.93
3.0	24 – 29	4.94 - 5.69
2.6	22 – 23	5.70 - 5.74
2.4	20 – 21	5.75 - 5.79
2.0	14 – 19	5.80 - 6.95
1.6	12 – 13	6.96 - 7.00
1.4	10 – 11	7.01 - 7.05
1.0	0 – 9	> 7.05

It should be noted that the standard operating procedures for collection and analysis of benthic macroinvertebrates used by NCDENR (2011) and TDEC (2012) are similar for EPT richness/abundance and taxa richness/abundance. TDEC (2012) uses the NCBI as part of their total biotic integrity index score and does not use bioclassification scores.

2.2.4 Identification of Collocated Survey Site Sets

In order to explore whether there were relationships among stream water quality (chemistry parameters), and trout and macroinvertebrate biotic metrics within the I&M program data, stream survey sites needed to be collocated. GIS was used to determine collocated sites, applying the following matching criteria: 1) no tributary or confluence between collocated sites, and 2) the distance between sites was less than 400 m. A total of 75 collocated pairs were found; however, only 23 survey site sets were collocated among all three program datasets (Fig. 5). Collocated survey sites included the following matches:

- Matched water quality, fish, and macroinvertebrate survey sites = 23 sets of sites
- Matched water quality and fish survey sites = 24 sets of sites
- Matched water quality and macroinvertebrate survey sites = 20 sets of sites
- Matched fish and macroinvertebrate survey sites = 8 sets of sites

Details on stream survey site locations, site names, and survey period of record of collocated site sets can be found in Appendix 2. Most collocated site sets were located with an elevation range between 1000 ft (305 m) and 4000 ft (1220 m) (Fig. 6). Only seven collocated stream survey site sets were at an elevation above 4000 ft.

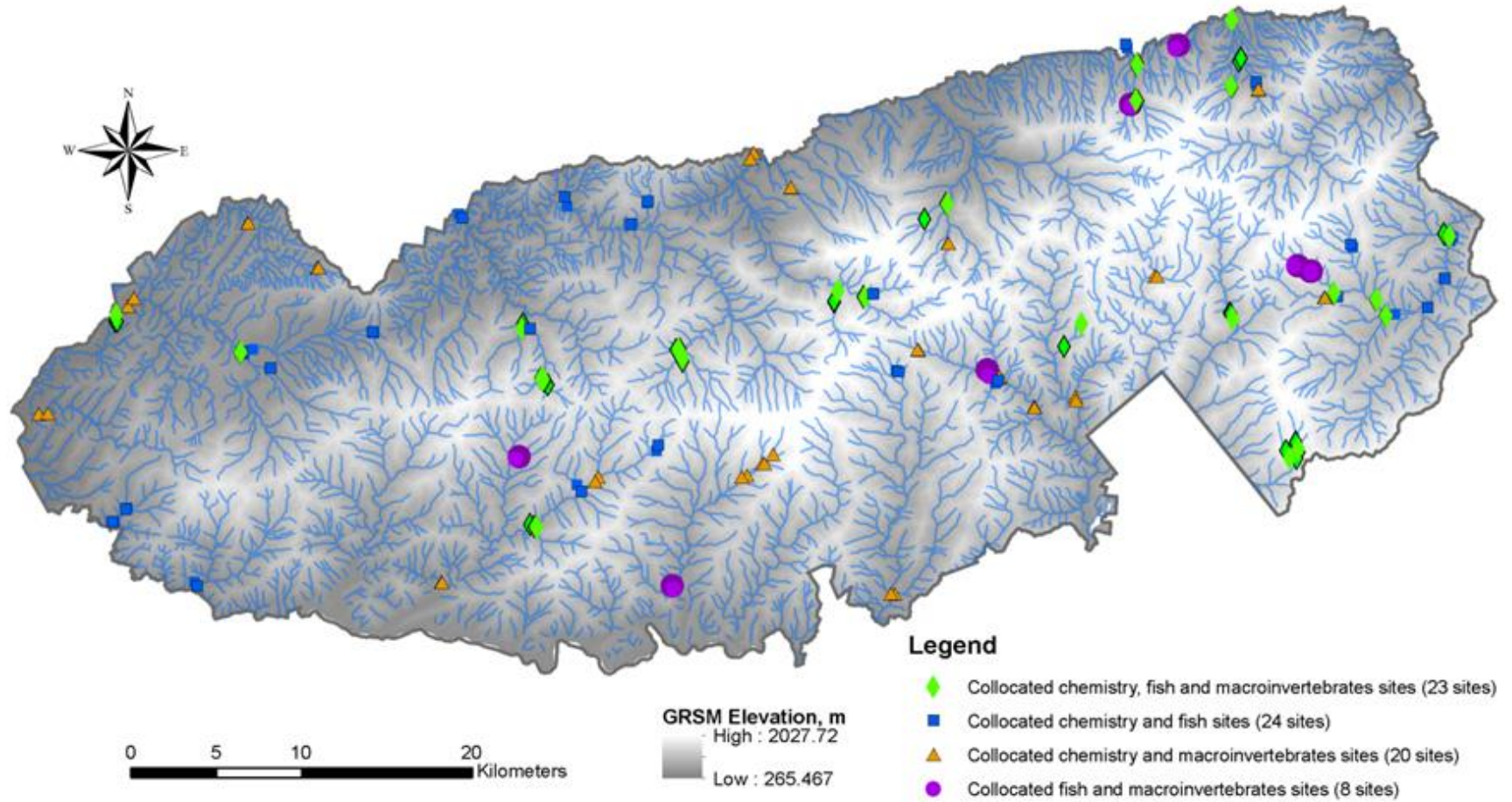


Figure 5. Collocated water quality, fish (trout), and benthic macroinvertebrates stream survey sites in Great Smoky Mountains National Park for data collected between 1993 and 2009. Note: each survey site is represented by a single symbol as noted in the legend, and collocated pairs are represented by two symbols in proximity.

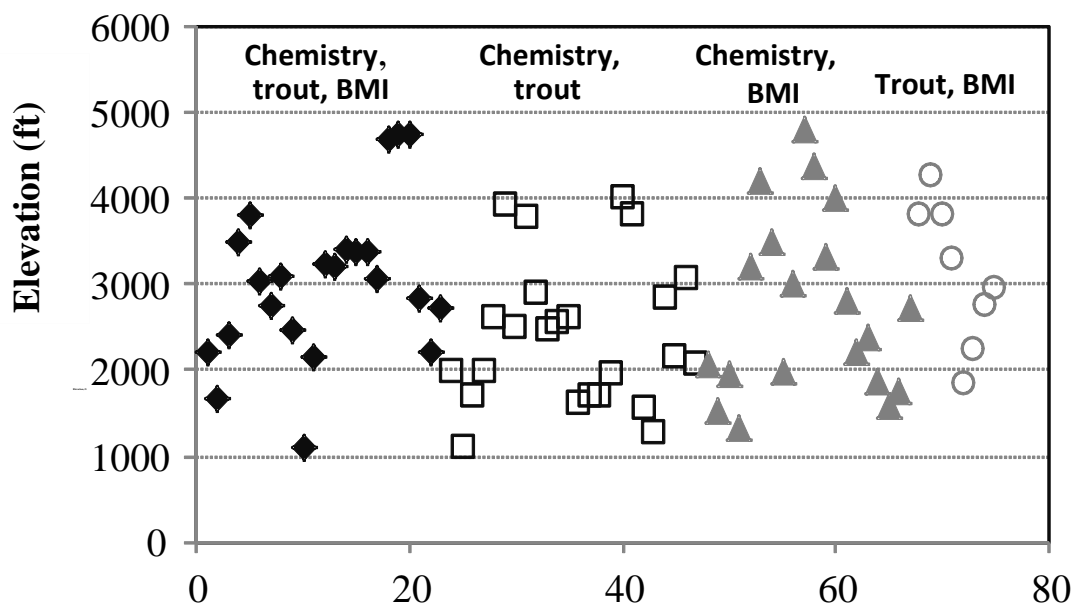


Figure 6. Summary of collocated stream survey sites and elevation in GRSM for 1993-2009 data. X-axis is the site-pair sequence number (Appendix 2). Collocated legend: chemistry, trout, and benthic macroinvertebrate (BMI) sites = ♦ (numbers 1-23 in Appendix 2); collocated chemistry and trout sites = □ (numbers 24-47); collocated chemistry and BMI sites = ▲ (numbers 48-67); collocated trout and BMI sites = ○ (numbers 68-75).

2.2.5 Identification of 303(d) Listed Streams

Based on the complete park-wide stream survey dataset, 12 streams were identified with pH measurements below 6.0 (Fig. 1, Table 2). Water quality standards for the states of North Carolina and Tennessee require a pH between 6.0 and 9.0 for wadable streams. The Tennessee Department of Environment and Conservation (TDEC) also requires that there be no pH change over one unit within a 24 hour period (TDEC, Chapter 1200-4-3). Water quality, fish, and macroinvertebrate datasets were evaluated for site collocation among the 303(d) listed streams per segment and data collection period (Table 2). A separate statistical analysis was conducted on the 303(d) listed streams only.

2.3 Baseflow-Stormflow Determination

Because of the regular interval for water quality monitoring, no attempt was made to collect water samples based on baseflow or stormflow stream conditions. However, water quality is highly dependent on flow condition, as stream water becomes more acidified during stormflow events (Cook et al. 1994, Deyton et al. 2009, Neff et al. 2013). Water quality samples and resulting chemistry were classified as either a baseflow or stormflow sample by using historic precipitation data from weather stations in or near GRSM (Fig. 7). Precipitation data were compiled from 20 weather stations operated by the National Oceanic and Atmospheric Administration (NOAA), the National Park Service (NPS), the National Atmospheric Deposition Program (NADP), and the Tennessee Valley Authority (TVA) (Appendix 3). Using GIS, the weather station nearest to the stream survey site was located and used to check precipitation records for each sample date. Per sample date, if a rainfall event lasting over six hours with an average hourly precipitation rate of 0.05 inch or greater occurred within 48 hours of the sample,

then that water quality sample was classified as stormflow. Otherwise, the water quality sample was classified as baseflow. Based on these criteria, about 24% of stream survey samples were classified as stormflow. This baseflow-

Table 2. Stream survey site sets for water quality, fish, and macroinvertebrates collocated in GRSM 303(d) listed streams, per stream segment and data collection period.

No.	303(d) Listed Stream Name	Fish Sites	Macroinvertebrate Sites	Stream Survey Sites
1	A tributary of Fish Camp Prong	None	None	None
2	Goshen Prong	None	None	None
3	Road Prong	From upstream to downstream: RPR-5, RPR-4, RPR-3, RPR-2, RPR-1	WPRP01	234, 71
4	Cannon Creek	CAN-2, CAN-1	MPCA01	47
5	Lowes Creek	None	None	None
6	Shutts Branch	None	MPSP01	None
7	Eagle Rocks Prong	None	None	None
8	Buck Fork	None	None	None
9	Copperhead Branch	None	None	104
10	Otter Creek	None	None	103
11	Inadu Creek	None	None	138
12	Rock Creek	From upstream to downstream: ROC-7, ROC-6, ROC-5, ROC-4, ROC-3, ROC-2, ROC-1	CBRC02, CBRC01	137

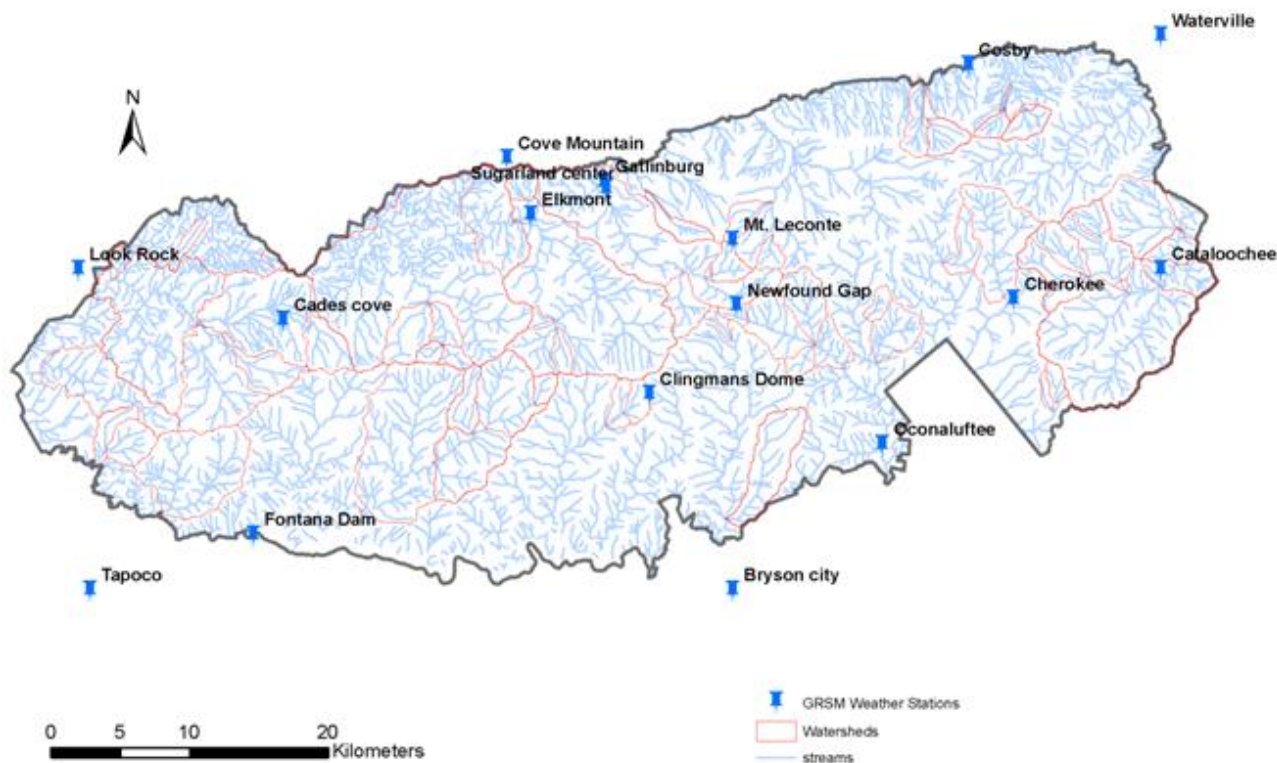


Figure 7. Weather stations located in or near GRSM. Watersheds used in this study are delineated in red.

stormflow classification appeared to be reasonable, but one should be conscious of the approach used in this study when interpreting the statistical results.

2.4 Dissolved Aluminum Concentrations: Parameter Estimations

Dissolved aluminum is a key water quality parameter associated with stream acidification because it can occur in much greater concentrations than other dissolved metals, but most importantly it can be toxic to aquatic organisms in the inorganic monomeric forms (Postek et al. 1995, Driscoll et al. 2003, Baldigo et al. 2007). In this portion of the study, three tasks were conducted. First, because dissolved aluminum was only analyzed in water samples from 2003 to the present, a means to predict dissolved aluminum concentrations for the water quality data prior to 2003 was needed in order to comprehensively correlate it with biological data collected prior to 2003. Second, Lawrence et al. (2009) suggested that base cation surplus (BCS) may be a good predictor of dissolved aluminum concentrations in acidified streams; therefore, a predictive relationship between dissolved aluminum concentrations and BCS was developed. Third, a geochemical equilibrium model was used to estimate what percentage of dissolved aluminum concentrations would be in the toxic forms of inorganic monomeric aluminum (Al_{IM}).

2.4.1 Estimating Dissolved Aluminum Concentrations

Using the dissolved aluminum data from 2003 through 2009, a stepwise multiple regression procedure was completed in JMP v.9 to develop a predictive model for dissolved aluminum. A statistically significant model was developed as follows:

$$[Al] = -0.0049 + 0.0010[SO_4^{2-}] + 0.0054[H^+] \quad N = 1322, p < 0.01, R^2_{adj} = 0.6329$$

where, the unit for SO_4^{2-} and H^+ is $\mu\text{eq L}^{-1}$ and the unit for aluminum is mg L^{-1}

This significant relationship suggests that stream aluminum concentrations may be controlled by external addition of sulfate by acid deposition, and proton concentrations produced through watershed biogeochemical processes. Biogeochemical processes may include soil desorption of aluminum related to excessive sulfate concentrations in soil water.

2.4.2 Relationship between Base Cation Surplus (BCS) and Dissolved Aluminum

BCS is expressed as the difference between base cations and anions:

$$\text{BCS} = \text{total base cations} - \text{anions} - \text{RCOO}^-$$

where, RCOO^- represents the concentration sum of organic acids

In GRSM streams during baseflow, organic acid concentrations were found to be insignificant compared with inorganic anions, such as nitrates and sulfates (Deyton et al. 2009, Neff 2010). Baseflow samples constituted 76% of the total samples in the water quality monitoring database (Section 2.3); therefore, most samples were taken when organic acids were low. Other than a few water samples analyzed by Deyton et al. (2009) and Neff (2010) for dissolved organic carbon (DOC), a surrogate for organic acids, there were no long-term data on organic acid concentrations from the stream survey sites. Thus, computations of BCS were based on the assumption that organic acid concentrations were zero.

Based on GRSM water quality data from 2003 to 2009, BCS versus dissolved aluminum concentrations were significantly correlated when the BCS concentration was less than $50 \mu\text{eq L}^{-1}$ (Fig. 8). When the BCS concentration was greater than $50 \mu\text{eq L}^{-1}$, dissolved aluminum concentrations were below detectable limits with the ICP (assumed to be near zero). BCS

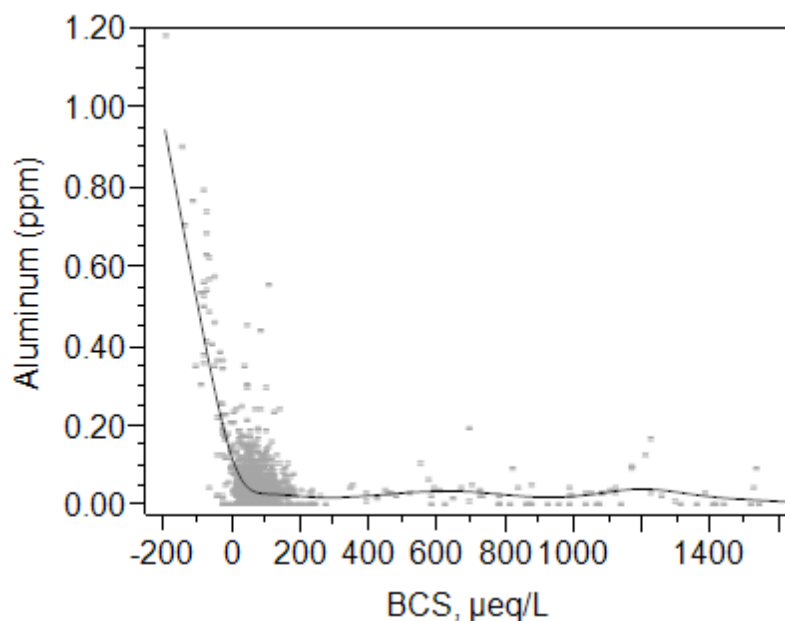


Figure 8. Base cation surplus (BCS, $\mu\text{eq L}^{-1}$) versus dissolved aluminum concentrations (Al, ppm) for GRSM water quality monitoring data from 2003 to 2009 (BCS < $50 \mu\text{eq L}^{-1}$; $n = 1451$; $R^2 = 0.62$; $p < 0.05$).

concentrations may be used to estimate dissolved aluminum concentrations by the following relationships:

$$\text{Al, ppm} = 0.2054 - 0.00417 \times \text{BCS} \quad \text{when BCS} < 50 \mu\text{eq L}^{-1}$$

$$\text{Al, ppm} = 0 \quad \text{when BCS} \geq 50 \mu\text{eq L}^{-1}$$

Although a relationship was found between dissolved aluminum and the BCS, dissolved aluminum concentrations were used in the statistical analysis examining water quality data for biotic effects associated with stream acidification.

2.4.3 Inorganic Monomeric Aluminum Estimation

In natural waters, dissolved aluminum is prone to speciation forming hydroxide complexes (e.g., $\text{Al}(\text{OH})_4^-$, $\text{Al}(\text{OH})_3$, $\text{Al}(\text{OH})_2^+$, AlOH^{2+}) in addition to sulfate, fluoride, and organic complexes (Burns 1989). Inorganic monomeric aluminum (Al_M) is a fractionated class of aluminum chemical species and is detected by specific laboratory protocols (Driscoll et al. 1980, Driscoll 1984). It consists mostly of alumino-hydroxide complexes, although Al^{3+} is considered the most toxic form to aquatic biota.

Because GRSM water quality samples were analyzed for dissolved aluminum only, inorganic monomeric aluminum must be estimated by use of a geochemical equilibrium model. Dissolved aluminum speciation was computed using the PHREEQC model (pH-REdox-EQuilibrium, in the C programming language). Using this model, organic aluminum complexes must be simulated in order to estimate the inorganic fraction. Because DOC or organic acids were not analyzed routinely in the samples, several assumptions had to be made to complete this modeling effort. The PHREEQC model assumptions used were as follows:

- The DOC concentration was assumed to be 0.75 mg L^{-1} for baseflow at all stream survey sites. This DOC concentration was based on a measured range between 0.5 and 1.0 mg L^{-1} from 34 measurements in eight watersheds (Neff 2010). Median DOC concentration was 0.75 mg L^{-1} .
- DOC was fractionated to be fulvic acid (40%) and humic acid (10%). These fractions were used as the average values for stream survey water samples.
- Molecular weights of fulvic acid and humic acid were assumed to be 650 g and 2000 g, respectively. The molecular weight is not a sensitive input variable in the model simulation; even if these weights were reduced by 10 times, there would be no significant change for the aluminum speciation distribution.
- Reaction equilibrium constants between organic acid and dissolved aluminum were obtained from cited literature (Burns 1989).

PHREEQC model simulations indicate that inorganic monomeric aluminum accounts for more than 96% of dissolved aluminum in most GRSM stream survey water samples. Species Al^{3+} will dominate the inorganic aluminum fraction for waters with a $\text{pH} < 5.0$. For stream water with a $\text{pH} > 6$, less than 1% of dissolved aluminum will be Al^{3+} . Species $\text{Al}(\text{OH})_2^+$ reaches a peak concentration at a pH of 6, gradually reducing in concentration, and changing to $\text{Al}(\text{OH})_4^-$ for stream water between pH 6 and 7. Based on model results, the use of measured dissolved

aluminum concentrations for a park-wide toxicological assessment provides an acceptable surrogate for inorganic monomeric aluminum. PHREEQC codes used in the model simulations are in Appendix 4.

2.5 Watershed Characteristics for Collocated Stream Survey Sites

Watershed characteristics for collocated stream survey sites were compiled for an exploratory statistical analysis of these characteristics with water quality and selected biotic metrics (Section 7.0). Watershed characteristics included drainage basin area, site elevation, average basin slope, stream order, channel density, soil hydraulic conductivity, and percent areas of soil types, vegetation classes, and surficial Anakeesta geology (Table 3). GIS data layers were obtained from the GRSM database web links (accessed 2011). To estimate spatial information for each survey site, the drainage basin boundary was delineated in ArcGIS using Spatial Analysis and ArcHydro tools. A total of 75 stream survey sites were found to be collocated, and watershed characteristics were compiled for these sites.

Because the number of potential variables for watershed characteristics were large ($n \approx 50$) compared to the number of chemistry sites ($n = 81$), a data mining effort was needed to reduce the set of predictor variables with high collinearity in order to obtain a statistically viable dataset. A three-step process was used for this data mining effort, in sequential order as follows: 1) inspection of variable relevance by professional judgment, 2) Pearson's correlation analysis, and 3) principal component analysis (PCA).

Individual watershed characteristic variables were examined for spatial distribution and relevance based on percent land cover. For example, the surficial geology layer was dominated by more than 97% Neoproterozoic rock (Appendix 5); therefore, the four other main surficial geological types found in GRSM become a spatially peripheral variable (Table 3). The same assessment was applied to remove several vegetation type variables including grape thicket, grassy bald, heath bald, treeless, and water, as well as soil type variables including entisols, rubble land, and slide area. The next step was to use a Pearson's correlation analysis to find variables that were significantly correlated with each other. For example, channel length was significantly correlated with basin area; therefore, in this case channel length was removed from the final variable list. PCA was used to assess correlations among the vegetation and soil type variables per eigenvector loading factors (Appendix 6). For example, the PCA plot for soil types indicated that the first two component axes explained 99.88% of soil variance. Axis component 1 was aligned with humic-typic dystropepts and axis component 2 was aligned with inceptisols-ultisols. Therefore, only these two soil type variables were retained for statistical analysis relating watershed characteristics with water quality and biotic metrics. The final result from the data mining effort was the selection of 20 watershed variables used for statistical analysis of water quality effects on aquatic biota (identified in the right column 'Model Variables' in Table 3).

Table 3. Model variables of watershed characteristics used in the study analyses, selected from candidate variables per statistical correlation analysis and principal components analysis.

Candidate Variables	Inspection and Correlation Analysis	Principal Components Analysis	Model Variables
Topography group:			
Basin Area, km ²			▪ Basin Area ▪ Site Elevation ▪ Stream Order ▪ Channel density ▪ Hydraulic Conductivity
Site_Elevation, m			
Stream order			
Channel length, m	correlated with basin area		
Channel density, m/km ²			
Hydraulic conductivity, m/s			
Elevation group:			
Ele_MIN, m	correlated with site elevation		▪ Mean elevation
Ele_MAX, m	insignificant correlation with chemistry		
Ele_RANGE, m			
Ele_MEAN, m			
Ele_STD, m	insignificant correlation with chemistry		
Slope group:			
Slope_MIN	insignificant correlation with chemistry		▪ Mean slope
Slope_MAX			
Slope_RANGE			
Slope_MEAN			
Slope_STD	insignificant correlation with chemistry		
Anakeesta group:			
Anakeesta area, m ²	correlated with basin area		▪ % of Anakeesta
% of Anakeesta			
Vegetation group: (expressed as percent of land coverage)			
Background	insignificant coverage		▪ Cove_Hardwood ▪ Mesic_Oak ▪ Mixed_Mesic_Hardwood ▪ Northern_Hardwood ▪ Pine ▪ Pine_Oak ▪ Spruce_Fir ▪ Tulip_Poplar ▪ Xeric_Oak ▪ VDif
Cove_Hardwood			
Grape_Thicket	insignificant land coverage		
Grassy_Bald			
Heath_Bald			
Mesic_Oak (hardwood)			
Mixed_Mesic_Hardwood			
Northern_Hardwood			
Pine (softwood)			
Pine-Oak (hardwood)			
Spruce_Fir (softwood)			
Treeless	insignificant coverage		
Tulip_Poplar (hardwood)		insignificant	

Candidate Variables	Inspection and Correlation Analysis	Principal Components Analysis	Model Variables
Water	insignificant coverage		
Xeric_Oak (hardwood)			
Hardwood	correlated to softwood, represented by VDif		
Softwood	correlated to softwood, represented by VDif		
VDif = Hardwood - Softwood			
Soil-type group: (expressed as percent of coverage)			
Entisols	insignificant coverage		▪ SDif ▪ Humic-typic Dystrudepts
Inceptisols	correlated to Ultisols, represented by SDif		
Rubble land	insignificant coverage		
Slide area	insignificant coverage		
Ultisols	correlated to Inceptisols, represented by SDif		
SDif =Inceptisols - Ultisols			
Humic Dystrudepts		insignificant	
Typic Dystrudepts			
Typic Hapludults			
Humic-typic Dystrudepts			
Rock-type group: (percent of land coverage)			
Paleozonic Rock	insignificant coverage		None
paleozoic and neoproterozoic dikes and sills			
Mesoproterozoic Rocks			
Neoproterozoic rock	dominant type		

3.0 Data Summaries: Water Quality and Aquatic Biota

Data summaries for water quality, fish, and benthic macroinvertebrates were compiled from the stream survey sites. Available data between 1990 and 2009 were summarized, with the aquatic biota collections beginning in 1990 and the water quality samples beginning in 1993 (Section 2.2). This chapter characterizes stream condition for this long-term monitoring period as background in the overall study's assessment of biological effects of water quality. The summaries can be used in the future to compare with a new set of long-term monitoring data. It cannot be used to assess whether various conditions are improving or worsening; this was done in the temporal trend analyses in Chapter 5.

3.1 Water Quality Data

Water chemistry data collected at each survey site for each date were delineated as baseflow or stormflow by methods described in Section 2.3. Median values of measured chemical parameters for baseflow and stormflow are summarized for each site in Appendix 7. Water chemistry varied greatly among samples; therefore, the mean and median descriptive statistics have less interpretative value than the min/max ranges (Table 4). In terms of stream acidification, survey sites in the Abrams Creek watershed exhibit high pH and ANC because the carbonaceous geology provides chemical buffering capacity to acid inputs. Survey sites in the sandstone geology are the most susceptible to acidification from acidic deposition.

Minimum pH and ANC during baseflow (4.44 and $-28.32 \mu\text{eq L}^{-1}$, respectively) were greater than during stormflow periods (4.39 and $-39.48 \mu\text{eq L}^{-1}$, respectively) (Table 4). Mean pH values for baseflow and stormflow within the entire water quality monitoring dataset (1993-2009) were 6.52 and 6.41, respectively, and mean ANC for baseflow and stormflow within the entire dataset was $68.27 \mu\text{eq L}^{-1}$, and $57.86 \mu\text{eq L}^{-1}$, respectively. During baseflow among all 387 stream survey sites, median pH was below 6.0 at 47 sites, and below 5.0 at 10 sites. The 10 stream sites below a median pH of 5.0 were site ID numbers: 53, 79, 92, 94, 95, 112, 113, 219, 237, and 360 (Table 5), and were mostly located in high-elevation watersheds (Fig. 9). During stormflow, median pH was below 6.0 at 51 sites, and below a pH of 5.0 at 13 sites. The 13 sites with a median pH below 5.0 during stormflow included the 10 sites listed above for baseflow conditions and three additional sites (218, 252, and 361). Among these 13 most acidified sites, only two sites currently are still monitored; they are sites 237 and 252. Sites 218 and 219 were monitored from 1994 to 2003, and the remaining nine sites were only monitored from 1993 to 1996.

This summary is for all sites, providing only general background information and not to be used for interpretation of biological effects on water quality. Within this context, during baseflow, mean sulfate, nitrate, and chloride concentrations were 37.58, 16.12, and $14.52 \mu\text{eq L}^{-1}$, respectively (Table 4). Mean ammonia was $0.13 \mu\text{eq L}^{-1}$, and mean BCS was $88.69 \mu\text{eq L}^{-1}$. The dominant base cation contributing to the BCS was calcium with a mean concentration of $75.42 \mu\text{eq L}^{-1}$. Mean concentration for dissolved aluminum was 0.06 mg L^{-1} .

Means for different water quality parameters generally were similar between baseflow and stormflow concentrations because of the sample variability as observed by standard deviations (Table 4). However, the maximum concentrations between baseflow and stormflow

concentrations provide for useful information. Within one standard deviation, chloride, sodium, calcium, and BCS

Table 4. Summary of stream chemical concentrations based on the median concentrations of 387 survey sites in GRSM from 1993 to 2009. Units for most ions are in $\mu\text{eq L}^{-1}$, except pH in pH units, conductivity (Cond) in $\mu\text{S/cm}$, and dissolved metals (Al, Cu, Fe, Mn, Si, Zn) in mg L^{-1} . Base cation surplus (BCS) is equal to [total base cations] – [anions] in $\mu\text{eq L}^{-1}$. Med = Median; Std = standard deviation.

		pH	ANC	Cond	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BCS	Al	Cu	Fe	Mn	Si	Zn
Base-flow	Med	6.63	49.23	14.02	13.93	11.53	30.41	35.61	0.00	10.56	23.51	55.29	70.03	0.04	0.00	0.02	0.00	2.44	0.01
	Mean	6.52	68.27	16.43	14.52	16.12	37.58	38.14	0.13	11.01	32.69	75.42	88.69	0.06	0.01	0.02	0.01	2.51	0.02
	Std	0.57	104.72	10.80	3.68	15.39	29.77	13.18	1.68	4.26	27.84	87.64	117.27	0.06	0.01	0.03	0.03	0.87	0.03
	Min	4.44	-28.32	6.96	2.57	0.00	5.20	8.64	0.00	3.19	6.72	18.60	-45.30	0.01	0.00	0.00	0.00	0.77	0.00
	Max	7.88	1109.4	118.2	53.75	89.32	297.63	118.2	32.27	34.67	221.59	882.83	1081.20	0.45	0.11	0.23	0.26	4.51	0.16
Storm-flow	Med	6.47	43.97	13.77	13.55	15.02	34.79	34.27	0.00	11.03	25.79	62.61	67.82	0.04	0.00	0.02	0.00	2.45	0.01
	Mean	6.41	57.86	15.93	14.14	18.20	43.12	36.16	0.07	11.90	33.63	76.09	80.41	0.06	0.00	0.02	0.01	2.44	0.02
	Std	0.60	78.11	8.33	3.22	16.25	35.76	12.44	0.45	6.18	26.33	60.09	85.94	0.06	0.01	0.02	0.05	0.68	0.03
	Min	4.39	-39.48	7.02	7.77	0.00	5.83	14.02	0.00	2.38	7.16	16.40	-112.44	0.00	0.00	0.00	0.00	1.28	0.00
	Max	7.75	706.43	78.80	28.38	87.22	361.51	83.76	4.67	55.39	253.48	559.73	733.00	0.41	0.08	0.10	0.38	4.41	0.16

Table 5. GRSM stream survey sites with a median pH below 5.0. Site locations reported by latitude/longitude are in Appendix 1.

Site ID	Description	Elevation (ft/m)	Monitoring Period
53	Surry Creek (Roaring Fork)	4435 (1352)	1993-1996
79	Alum Cave Creek above Styx Branch	4280 (1305)	1993-1996
92	Unnamed trib to Ramsay Prong below falls	4280 (1305)	1994-1996
94	Ramsey Prong above falls	4480 (1366)	1993-1994
95	Upper Ramsey Prong	5000 (1524)	1993-1994
112	Buck Fork on AT near Tricorner Knob	6120 (1865)	1994-1996
113	Ramsey Prong on AT near Mt. Guyot	6500 (1981)	1994-1996
218	Spring at Silers Bald Shelter	5440 (1658)	1994-2003
219	Double Spring Gap Shelter (NC site)	5510 (1679)	1994-2003
237	Walker Camp Prong at last bridge	4510 (1375)	1993-2009
252	Beech Flats below roadcut	4760 (1451)	1993-2009
360	Upper Walker camp	4710 (1436)	1993-1995
361	Forney Creek (Clingmans Dome)	6240 (1902)	1995-1996

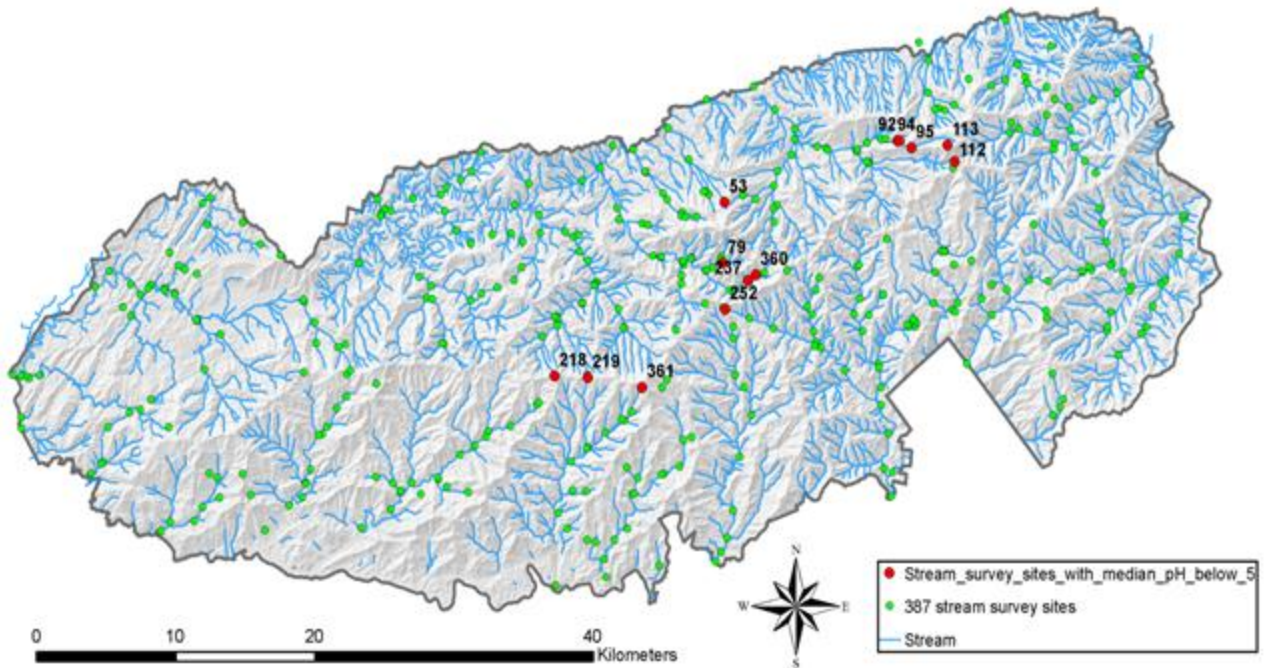


Figure 9. Stream survey sites in GRSM with median pH below 5.0 for the entire water quality dataset from 1993 to 2009.

concentrations were less during stormflow than baseflow conditions, indicating a dilution of these ions during greater stream discharges. Maximum nitrate and total aluminum concentrations did not differ. Maximum sulfate and potassium concentrations were greater during stormflow than baseflow conditions, potentially indicating increased ion transport during stormflow periods.

3.2 Fish Data

Fish metrics for brook and rainbow trout included density (number/100 m²), biomass (kg/ha), and the condition factor K, and were summarized for 298 stream survey sites from 1990 to 2009 (Table 6, Appendix 8). Median values of the fish metrics were computed per stream survey site (Appendix 8). Summary data (Table 6) cannot be used to assess whether various conditions are improving or worsening; this was done in the temporal trend analyses in Chapter 5. However, summary data can be used in the future to compare with a new set of long-term monitoring data.

In general, brook trout densities were about twice that of rainbow trout, for both YOY and adults (Table 6). Brook trout YOY median density was 3.39 fish/100 m² and adult density was 5.87 fish/100 m². Rainbow trout YOY median density was 0.98 fish/100 m² and adult density was 2.95 fish/100 m². Despite the density differences between these two species, biomass differences were less than 5%. Median adult biomass for brook and rainbow trout was 14.69 and 13.56 kg/ha, respectively. With respect to the condition factor K, brook trout had slightly smaller median K values (0.98, 0.96) than rainbow trout (1.02, 0.97) for both YOY and adults. The overall median K value was about equal to 1.00.

3.3 Benthic Macroinvertebrate Data

Benthic macroinvertebrate metrics were computed for a total of 118 stream survey sites from 1990 to 2003, including descriptive statistics on the individual metrics (Table 7). Metrics included: NCBI

Table 6. Summary of brook and rainbow trout density, biomass, and condition factor K for GRSM stream survey sites per individual collections during the period 1990 to 2009. Dens = fish/100 m², Biomass = kg/ha.

		Young of the Year (YOY)			Adult		
		Density	Biomass	K	Density	Biomass	K
Brook Trout (N = 1269)	Median	3.39	0.94	0.98	5.87	14.69	0.96
	Mean	5.54	1.55	0.99	8.06	18.25	0.96
	SD	6.18	1.84	0.13	8.03	15.88	0.07
	Minimum	0.00	0.00	0.51	0.00	0.00	0.66
	Maximum	49.99	21.49	1.76	51.83	114.63	2.07
Rainbow Trout (N = 963)	Median	0.98	0.18	1.02	2.95	13.56	0.97
	Mean	2.39	1.11	1.02	3.71	15.84	0.97
	SD	3.36	2.26	0.14	3.36	13.13	0.08
	Minimum	0.00	0.00	0.55	0.00	0.00	0.61
	Maximum	24.50	22.49	1.75	19.17	65.45	1.95

Table 7. Summary of benthic macroinvertebrate metrics for GRSM stream survey sites per individual collection during the period 1990 to 2003 (N = 396).

Macroinvertebrate metrics		Median	Mean	SD	Min	Max
NCBI		2.20	2.31	0.60	0.86	4.55
EPT richness		30	30.62	7.44	4	56
EPT % abundance		0.74	0.73	0.11	0.31	0.99
Bioclassification		4	4.29	0.48	3	5
Taxa richness		50	53.55	16.34	10	113
Taxa abundance		330	356.45	180.86	27	1219
Richness of functional feeding groups	Collector-Filterer	7	7.48	2.53	1	16
	Collector-Gatherer	12	13.07	6.30	0	34
	Predator	15	15.17	4.82	3	36
	Scraper	8	8.58	3.32	2	20
	Shredder	7	7.40	2.08	2	15
	Unknown	1	1.87	1.84	0	10
Abundance of functional feeding groups (%)	Collector-Filterer	17.89	18.92	8.03	0.37	55.56
	Collector-Gatherer	24.14	24.64	9.71	0.00	62.44
	Predator	20.82	20.77	6.32	5.80	44.44
	Scraper	14.08	14.78	6.36	0.00	33.33
	Shredder	17.41	19.09	8.52	2.82	63.68
	Unknown	0.85	1.80	2.41	0.00	14.81

(North Carolina Biotic Index), EPT (Ephemeroptera, Plecoptera, Trichoptera) richness and abundance, bioclassification, taxa richness and abundance, and richness and abundance of functional feeding groups. The complete data summary per stream survey site is in Appendix 9. The mean NCBI was 2.31, and streams with this score (i.e., < 4.00) in mountain regions are considered to be in excellent condition with regard to biotic integrity (NCDENR 2011). The maximum NCBI was 4.55,

which is considered as “good” condition. The mean EPT species richness was 30.62, which is a “good” classification for mountain regions, and was 57% of the mean taxa richness. The final bioclassification score, derived from both EPT richness and the NCBI, was 4, which again was a rating of “good.” Bioclassification scores found that no streams in GRSM surveys were considered biologically impaired. With respect to the functional feeding groups, percent individual numbers for collector-gatherer, predator, collector-filterer, scraper, and shredder were 24.1%, 20.8%, 17.9%, 14.1% and 17.4%, respectively.

4.0 Toxicological Assessment and Biotic Sensitivity Maps

The survival, growth, and productivity of fish and macroinvertebrates are dependent upon environmental conditions related to water quality. Of most concern in GRSM are the effects of atmospheric acid deposition resulting in stream acidification, and the potential for biological impairment due to chronic and/or episodic acidity leading to toxic environmental conditions (Neff et al. 2009). A toxicological assessment of GRSM streams was conducted using toxicity threshold data for fish and macroinvertebrates compiled from an extensive literature review, and by comparing key toxicity thresholds with measured stream chemistry data at collocated sites. Comparisons with toxicity thresholds were completed for both baseflow and stormflow stream chemistries.

An exploratory analysis was completed with trout density data, where scatterplots were generated with stream chemistry concentrations. Because fish data were based upon a one-year sampling frequency and chemistry data was based on multiple samples annually, averaged chemistries were used for the period previous to the fish collection date, where YOY numbers were from a one-year period, and adult numbers were from a three-year period. Scatterplot patterns provide for the inspection of potential chemical thresholds in GRSM data, where abrupt drops in fish metrics occur at a specific chemical concentration. For each scatterplot, stream chemistry ranges were summarized for all collocated water quality and fish survey sites grouped by trout species (brook trout, rainbow trout) and age class (YOY, adult). These chemistry ranges were then applied to all water quality stream survey sites, generating a trout distribution map based on water quality data.

Biotic sensitivity maps were created in ArcGIS v.10.0 identifying stream survey sites within toxicity-threshold ranges, where ranges were determined as an outcome of the literature review. Sites exceeding toxicity thresholds are enumerated on the sensitivity maps, where site number descriptions and latitude/longitude are in Appendix 1. Sensitivity maps were generated for pH, ANC, and dissolved aluminum toxicity thresholds. Maps were generated for all 387 stream survey sites with historic water quality data (1993-2009), and the 43 survey sites currently monitored (2003-2009). A final analysis included generating a map of collocated water quality and fish sites from areas where no fish were found and where water quality indicated that conditions were unfavorable for fish occupancy.

4.1 Toxicity Thresholds: Literature Review Summary

Current published research on toxicity to fish and macroinvertebrates from stream acidification identifies pH, dissolved aluminum, and other dissolved metals as the dominant water quality parameters (Appendix 10). Protons, as measured by pH, can cause a loss of sodium and chloride across fish gills, disrupting ion regulation and leading to severe deficiency of extracellular ions and death (Spry and Wiener 1991, Courtney and Clements 1998). Most research has been conducted on salmonid species, including brook and rainbow trout at different life stages (Baldigo et al. 2009). Acid toxicity in brook trout causing asphyxia is reported to occur in the pH range of 5.5-6.4, and potential lethal effects occur in the range of 4.2-4.8 (Neville and Campbell 1988). Similarly, macroinvertebrates experience an ion loss through gills with decreases in stream pH (Felten and Guérol 2006). An extensive summary of cited toxicity literature is found in Appendix 10.

Toxicity from pH is classified as follows: 1) slight impairment = pH 5.5 to 6.4; 2) moderate impairment = pH 5.0 to 5.5; 3) severe impairment = pH 4.0 to 5.0; and 4) lethal = pH < 4.0 (Table 8). Tennessee water quality standards require a pH between 6.0 and 9.0 for wadable streams and no

Table 8. Summary of toxic effects of pH, and aluminum and zinc concentrations on salmonids (trout) and benthic macroinvertebrates from published literature (Appendix 10).

Chemical	Salmonids	Benthic Macroinvertebrates
pH		
5.5-6.4		Slightly impacted
5.0-5.5	Reduced growth	Moderately impacted <i>Baetis muticus</i> , <i>Heptagenia lateralis</i> and <i>R. semicolorata</i> absent (Ephemeroptera). Native mayfly <i>B. alpinus</i> declined.
4.0-5.0	Reduced abundance; adverse effect to mortality; harmful to the eggs and fry	Severely impacted; Lower taxonomic richness; Scarce Empididae (Diptera), <i>Isoperla rivulorum</i> (Plecoptera), <i>Rhithrogena</i> spp. and <i>Baetis</i> spp. (Ephemeroptera).
<4.0	Lethal to salmonids	Significantly fewer individuals and taxa; Reduced abundance resulted primarily from reduced abundance of mayflies.
Al		
Al _{tot} >0.2 mg/L	Loss of Na and Cl; Measureable reductions in survival and growth; Significant mortality of brook trout	Reduced density of Ephemeroptera and Ceratopogonidae (Diptera)
Al _{tot} >0.4mg/L		Acute toxicity LC ₅₀ for <i>Hyaella azteca</i> (Crustacea), <i>Pisidium</i> spp. (Bivalvia), <i>Enallagma</i> sp. (Odonata)
Al _{in} >0.2 mg/L		Mortality of <i>Gyraulus</i> sp. (Gastropoda), <i>Hyaella azteca</i> (Crustacea), chironomids (Diptera)
Zn		
>0.047 mg/L	Fish avoidance	
>0.11 mg/L		<i>Ceriodaphnia dubia</i> (Crustacea) abundance
>0.219 mg/L	Start to affect survival	reduced by 50%

change over 1.0 unit within a 24 hour period (TDEC, Chapter 1200-4-3). North Carolina standards for stream pH also are between 6 and 9. In general, streams with ANC less than 0 $\mu\text{eq L}^{-1}$ would be considered acidic, although TDEC recommends a target of 50 $\mu\text{eq/L}^{-1}$ for TMDL management. While pH has been the chemical parameter studied for toxicity thresholds, ANC provides useful assessment information on stream acidification condition.

Dissolved aluminum in the form of inorganic monomeric aluminum (Al_{IM}) is regarded as the most toxic dissolved metal for fish and macroinvertebrates in acidified stream waters (Driscoll et al. 1980, Driscoll 1985, Hermann et al. 1993). Fish gill ion transport is disrupted by replacing calcium on gill surfaces with increased concentrations of monomeric aluminum (Table 8). Increased monomeric aluminum can also cause excessive whole-body loss of sodium, resulting in loss of ion regulation (Appendix 10). Driscoll et al. (2001) suggests that monomeric aluminum concentrations above 2.0

$\mu\text{mol L}^{-1}$ as an appropriate threshold for toxicity. Others have suggested that in addition to a concentration threshold, a duration or dose threshold should be considered since stream acidification is episodic in nature (Gagen et al. 1993). Baldigo and Murdoch (1997) found significant mortality of brook trout when monomeric aluminum exceeded 0.20 mg L^{-1} for more than two days.

It should be noted that aluminum toxicity is dependent on the overall water chemistry, where monomeric aluminum can bind with organics reducing its toxicity (Driscoll 1985). Aqueous aluminum chemistry is described in Section 2.4.3, where through the use of a geochemical equilibrium model (PHREEQC), it was found that most of the dissolved aluminum measured in GRSM streams were in the toxic monomeric form; essentially Al^{3+} for stream pH units between 5 and 6. It was concluded that dissolved aluminum concentrations were a good surrogate measure for toxic monomeric aluminum. It should be noted that base cations in terms of water hardness may influence its toxicity on biota (Appendix 10); therefore, actual toxicity thresholds may vary from one watershed to another because of local water chemistry characteristics. Analysis of stream chemistry data also found that the dissolved aluminum concentration was essentially zero when the BCS concentration was greater than $50 \mu\text{eq L}^{-1}$, and directly correlated with the BCS concentration when less than $50 \mu\text{eq L}^{-1}$ (Section 2.4.2).

Other dissolved metals with toxicity thresholds for aquatic biota included copper (Cu), iron (Fe), and manganese (Mn); however, GRSM stream water concentrations of Cu, Fe, and Mn were far below the reported toxicity thresholds (Appendix 10). Therefore, only toxicity thresholds for pH, Al, and Zn were summarized for this assessment (Table 8). Zinc was included even though most concentrations were below 0.047 mg L^{-1} , and only a few exceedances occurred (Figs. 10-13). Water quality standards for Tennessee also include Criterion Maximum Concentration (CMC) and Criterion Continuous Concentration (CCC) for cadmium, copper, lead, nickel, silver, and zinc (TDEC, Chapter 1200-4-3). CMC and CCC levels for these metals generally were not a concern for GRSM (Barnett 2003).

4.2 Trout Density Compared with Stream Chemistry

Adult and YOY brook and rainbow trout densities (fish/100 m^2) were compared with stream chemistry for collocated sites (Figs. 10-13). To represent relevant water quality exposure periods as a function of trout life histories, average chemistries for YOY fish were obtained for one year prior to the fish collection dates, and average chemistries for adult fish were obtained for three years prior. Data patterns also provide for the inspection of whether a chemical threshold was potentially evident. For example, maximum fish densities, which represent an overall carrying capacity among GRSM streams, increased when pH was approximately above 6, whereas densities of “zero” occurred more often below pH 6.

Maximum brook trout densities compared with ANC concentrations were bell-shaped curves with maximum densities observed between 30 and $60 \mu\text{eq L}^{-1}$ for both YOY and adults (Figs. 10-11). Rainbow trout were found between 20 and $100 \mu\text{eq L}^{-1}$ ANC, although in Abrams Creek, ANC concentrations were measured above $1000 \mu\text{eq L}^{-1}$ with adults present (Figs. 12-13). Patterns for BCS were similar to those observed for ANC, where maximum densities for brook trout occurred at about $50 \mu\text{eq L}^{-1}$, and rainbow trout occurred between 50 and $100 \mu\text{eq L}^{-1}$. Maximum densities for brook trout declined when sulfate concentrations were greater than $35 \mu\text{eq L}^{-1}$, and they were not found in streams with sulfate above $70 \mu\text{eq L}^{-1}$. Rainbow trout also were not found in streams with

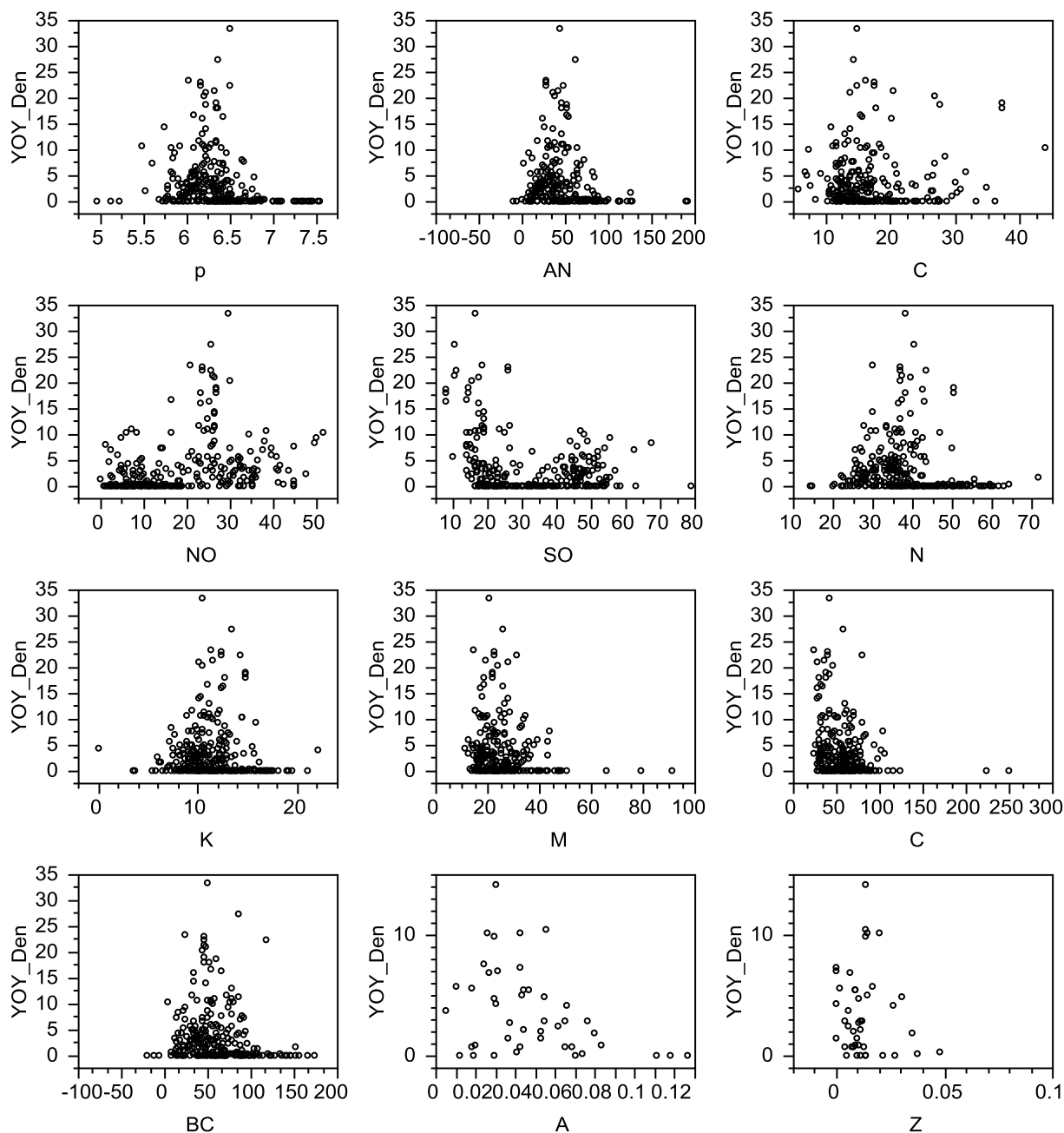


Figure 10. Brook trout YOY densities (fish per 100 m²) compared to water chemistry at collocated stream survey sites in GRSM between 1993 and 2009. Chemical concentrations reported as $\mu\text{eq L}^{-1}$ except pH as standard pH units, and Al and Zn as mg L^{-1} .

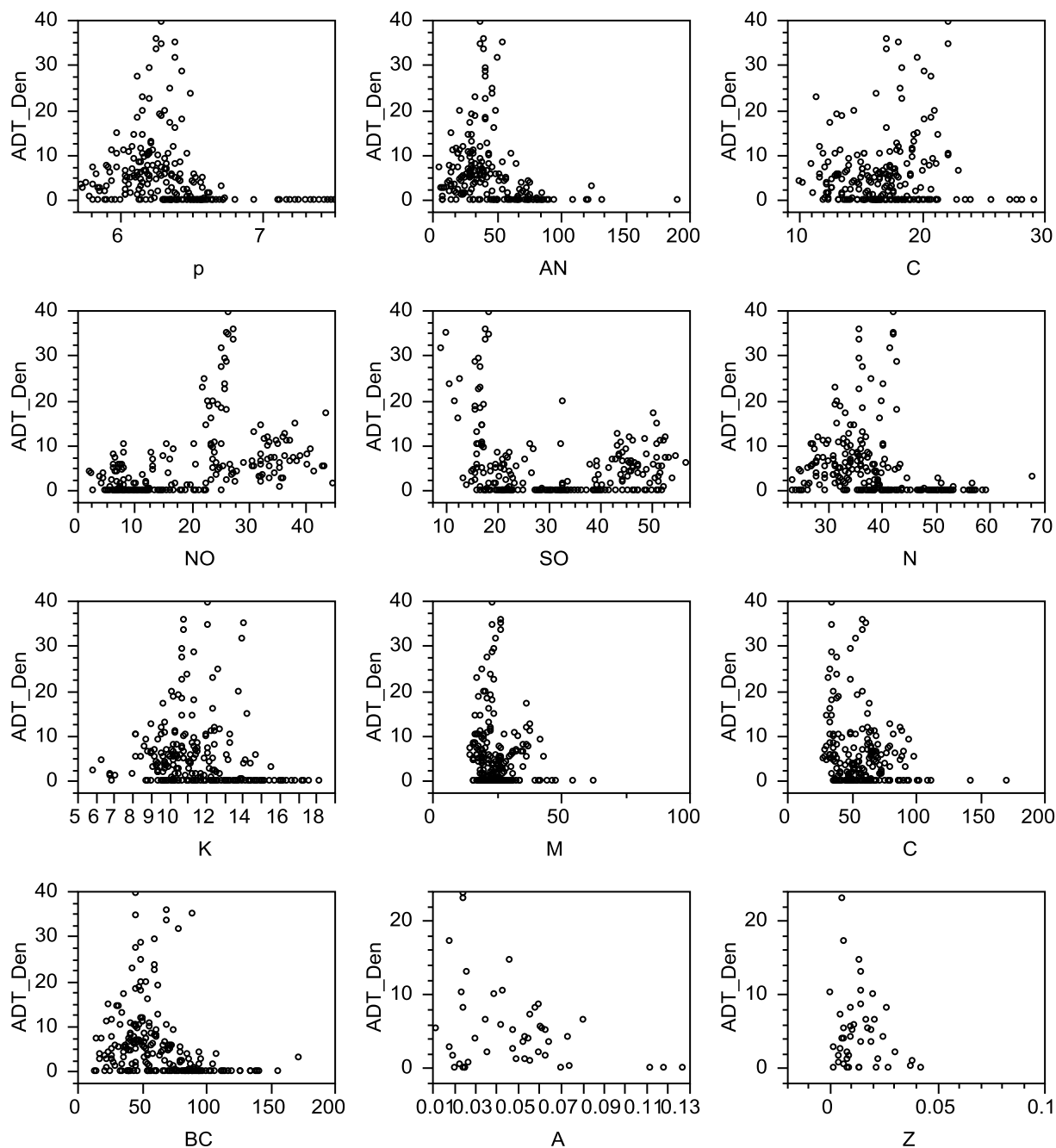


Figure 11. Brook trout adult densities (fish per 100 m²) compared to water chemistry at collocated stream survey sites in GRSM between 1993 and 2009. Chemical concentrations reported as $\mu\text{eq L}^{-1}$ except pH as standard pH units, and Al and Zn as mg L^{-1} .

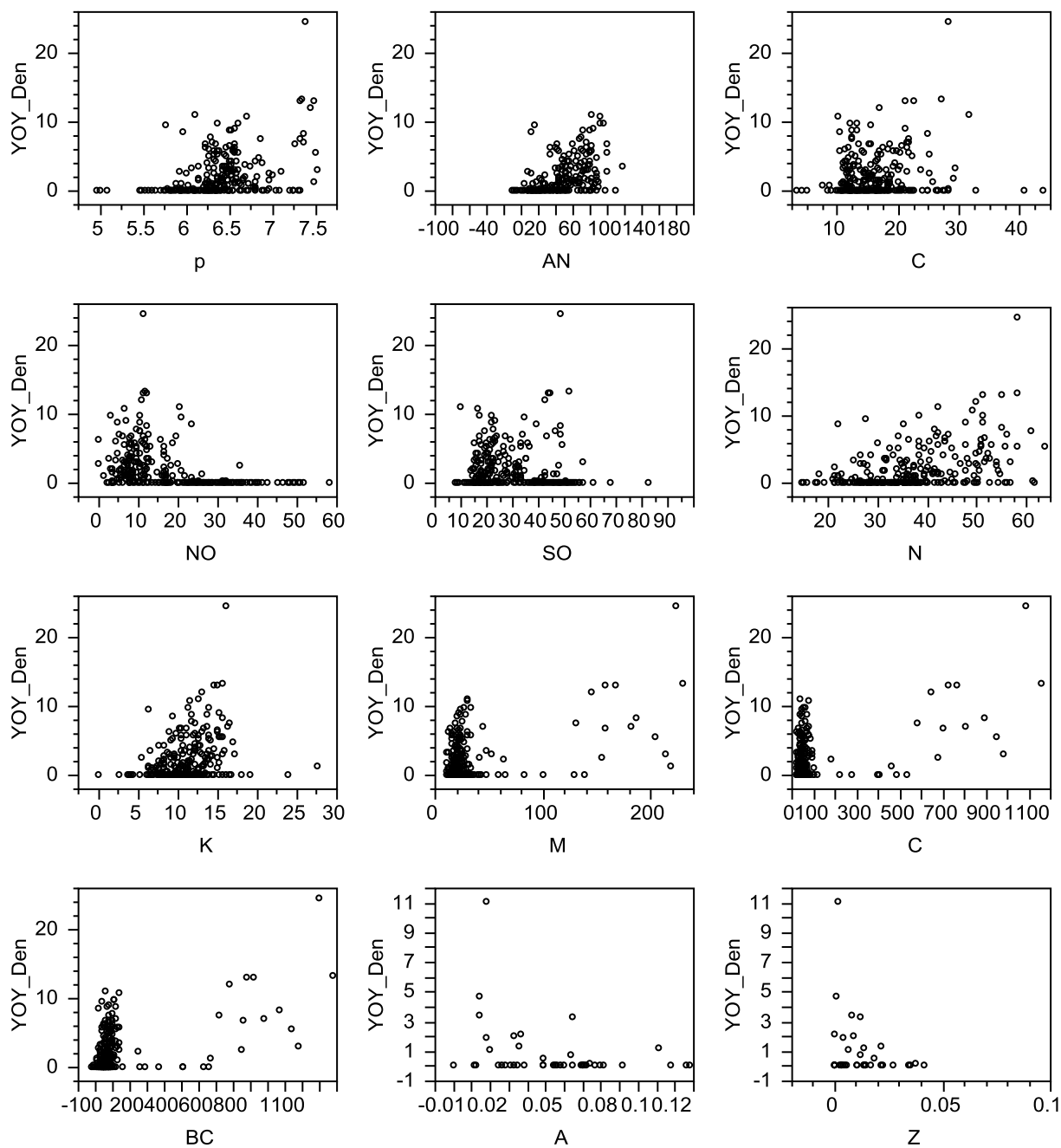


Figure 12. Rainbow trout YOY densities (fish per 100 m²) compared to water chemistry at collocated stream survey sites in GRSM between 1993 and 2009. Chemical concentrations reported as $\mu\text{eq L}^{-1}$ except pH as standard pH units, and Al and Zn as mg L⁻¹.

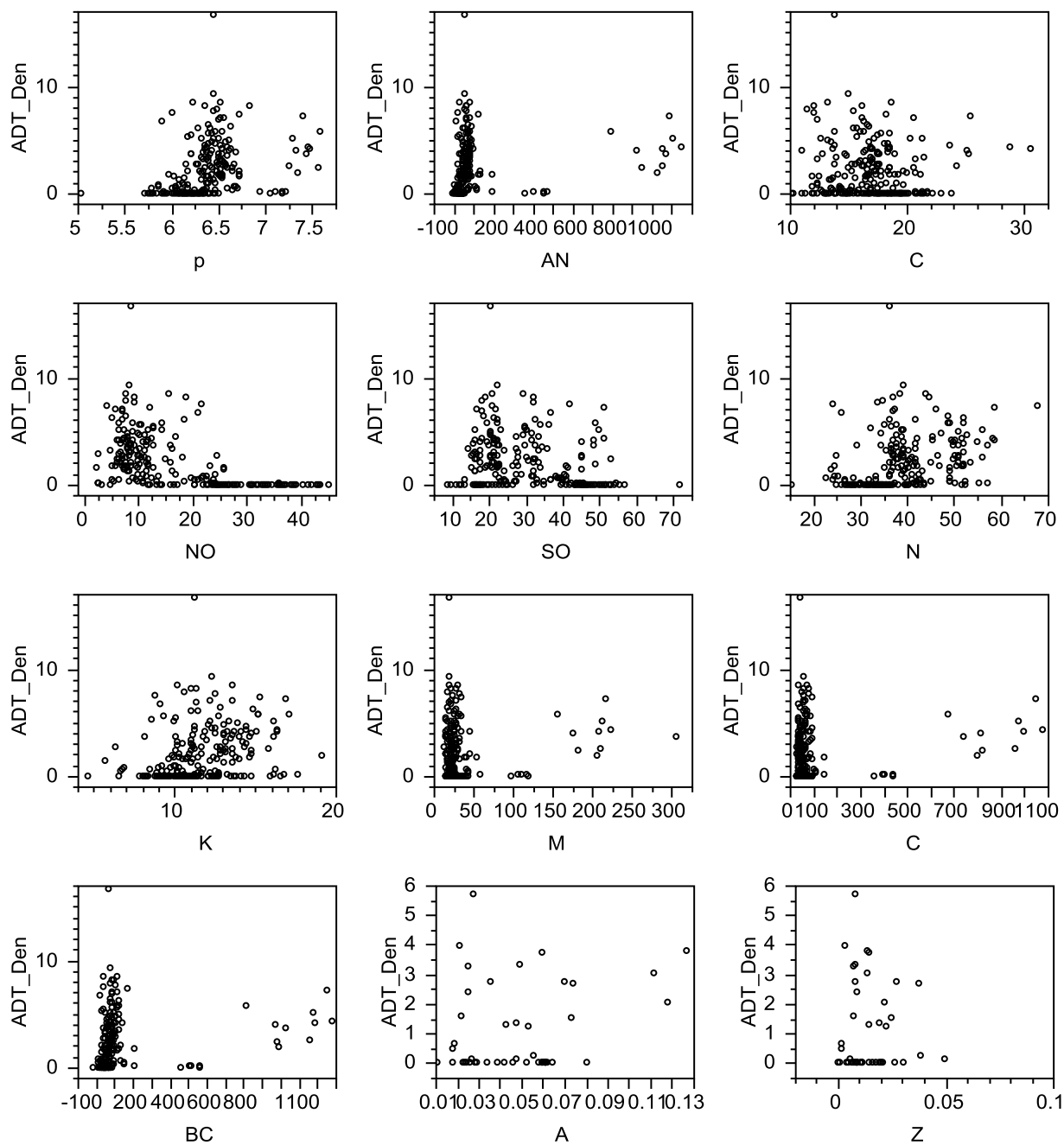


Figure 13. Rainbow trout adult densities (fish per 100 m2) compared to water chemistry at collocated stream survey sites in GRSM between 1993 and 2009. Chemical concentrations reported as $\mu\text{eq L}^{-1}$ except pH as standard pH units, and Al and Zn as mg L^{-1} .

sulfate above $70 \mu\text{eq L}^{-1}$. Adult brook trout densities increased with increasing sodium concentrations, whereas this pattern was not observed with adult rainbow trout. Adult brook trout densities appeared to decline to zero at levels of 0.08 to 0.09 mg L^{-1} for aluminum, while adult rainbow trout densities declined to zero when this value was greater than 0.13 mg L^{-1} . This observation for aluminum could represent toxicity thresholds, but must be considered speculative because data collection methods were not designed for a toxicological study with standard procedural controls.

Total ranges for pH and chemical parameters were reported for all of the collocated fish and water quality monitoring sites combined, allowing for an inspection of chemical thresholds. Although stream survey sites were reported with a pH of 5.0, brook trout were not collected at sites with a pH below 5.5, and rainbow trout were not collected below a pH of 5.8. Both brook and rainbow trout were not collected in streams having an ANC below $0 \mu\text{eq L}^{-1}$, which is a toxicity threshold consistent with literature (Appendix 10). Aluminum concentrations were summarized as described above, but they were slightly below the literature-suggested threshold of 0.20 mg L^{-1} .

4.3 Biotic Sensitivity Maps Based on Toxicological Thresholds

Toxicological thresholds determined to be critical for trout and macroinvertebrates included pH, ANC, and dissolved aluminum (Table 8, Appendix 10). In order to spatially observe locations of stream survey sites exceeding toxicological thresholds, the locations were mapped (Figs. 14-16). Site locations with water chemistries that exceed a toxicological threshold were considered watersheds potentially sensitive to supporting aquatic biota. Sensitivity maps were generated from median values for measurements taken from the 43 currently monitored stream survey sites (2003-2009), and from the 387 historical survey sites (1993-2009). Water quality data from the historical sites were mostly collected from 1993 to 1995. Although the historic data is more comprehensive and more spatially distributed throughout GRSM, it may not represent current conditions. This limitation does not interfere with the basic goal of this overall assessment, which is to identify current and historic sites with toxicological exceedances in order to support future I&M planning efforts.

Two of the 43 sites in the current water quality monitoring program, sites 237 and 252, were identified as having a pH less than 5.0, ANC less than $0 \mu\text{eq L}^{-1}$, and dissolved aluminum greater than 0.20 mg L^{-1} (Figs. 14-16). These sites, Walker Camp Prong (at last bridge) and Beech Flats (below road cut), contained chemistries that exceed toxicological thresholds (Table 8). Because the current monitoring program only includes 43 stream survey sites, with only two sites exceeding toxicological thresholds, it may not provide an accurate characterization of current park-wide conditions. Historically, several more stream survey sites were identified as exceeding pH, ANC, and aluminum toxicological thresholds. The key observation was that most sites exceeding these thresholds occurred in higher elevation streams of GRSM.

4.4 Trout Distributions Based on Water Quality Predictors

Brook and rainbow trout distributions in GRSM can generally be described as brook trout occurring in higher elevation streams and rainbow trout occurring in lower elevation rivers and streams, with the two populations overlapping in the mid-elevation range (Fig. 17). High-elevation headwater streams above 5000 feet (1524 m) typically have no fish. A predicted trout distribution map was generated based on the water chemistry ranges where trout species were

found, as defined in Table 9 compared with the water quality data for the stream survey sites. Based on this analysis,

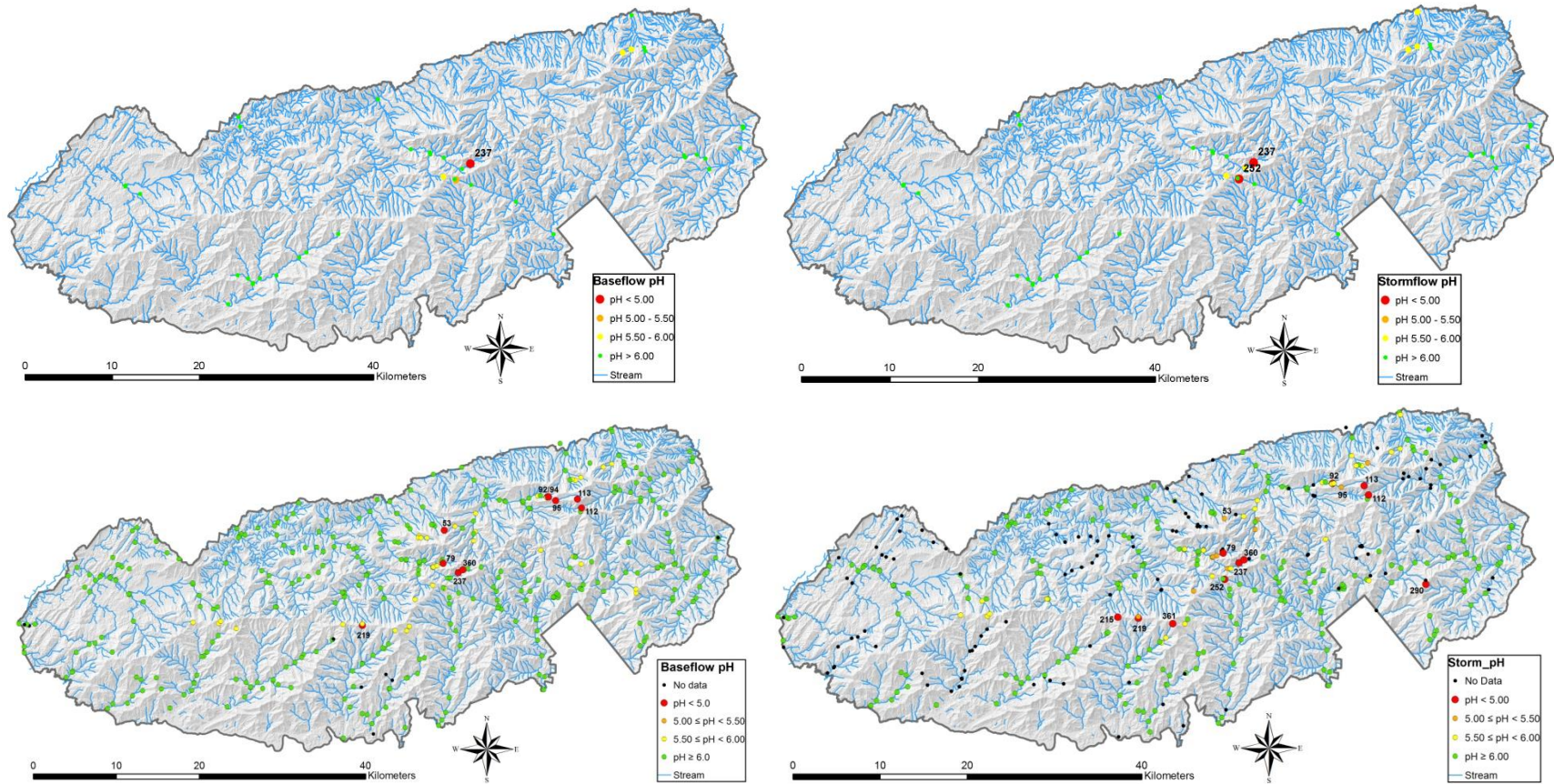


Figure 14. Median pH values during baseflow (left) and stormflow (right) conditions for the 43 currently monitored stream survey sites (upper) and 387 historical sites (lower) in GRSM from 1993-2009.

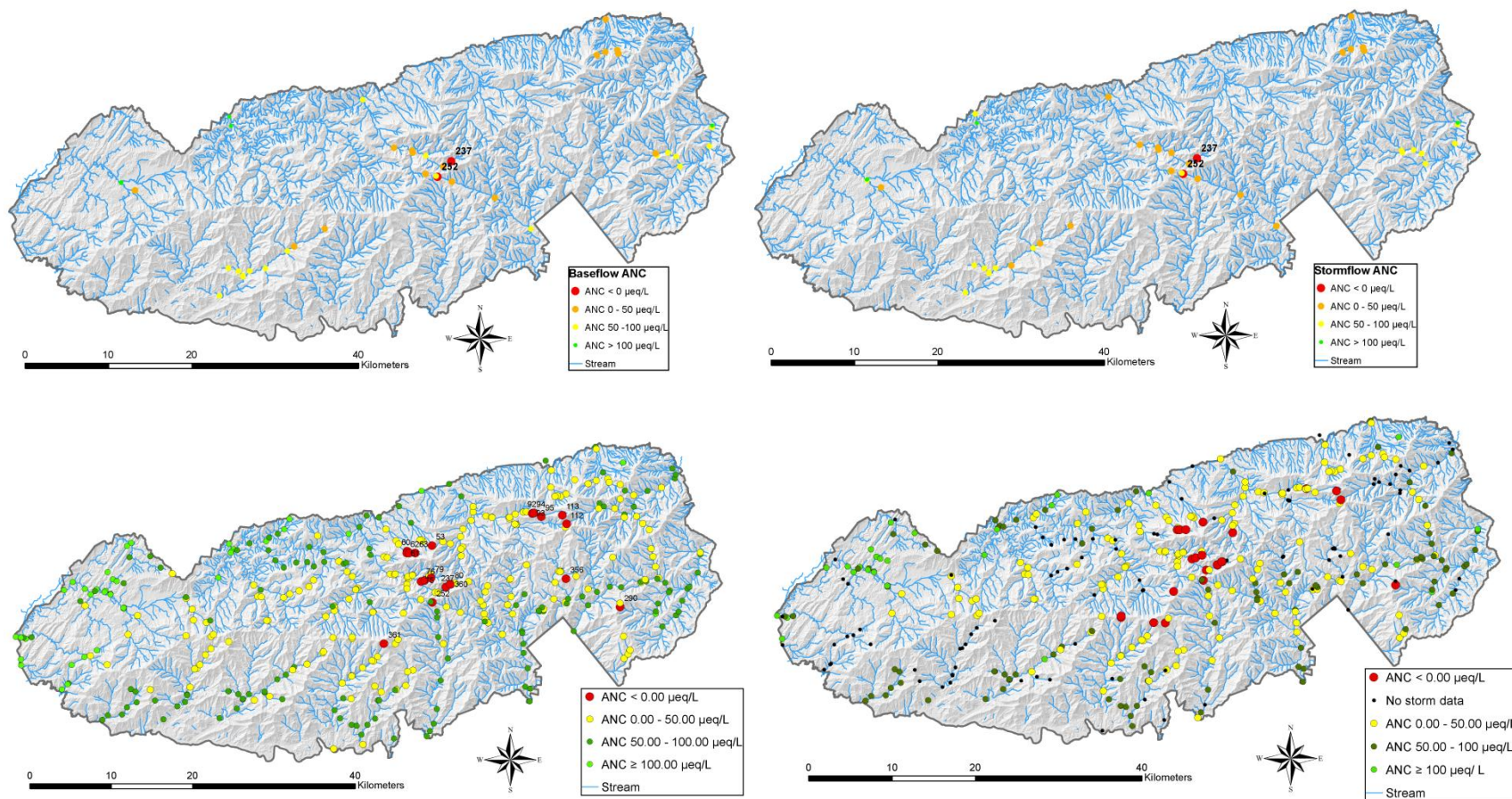


Figure 15. Median ANC concentrations ($\mu\text{eq/L}$) during baseflow (left) and stormflow (right) conditions for the currently monitored 43 stream survey sties (upper) and 387 historical survey sites (lower) in GRSM from 1993-2009.

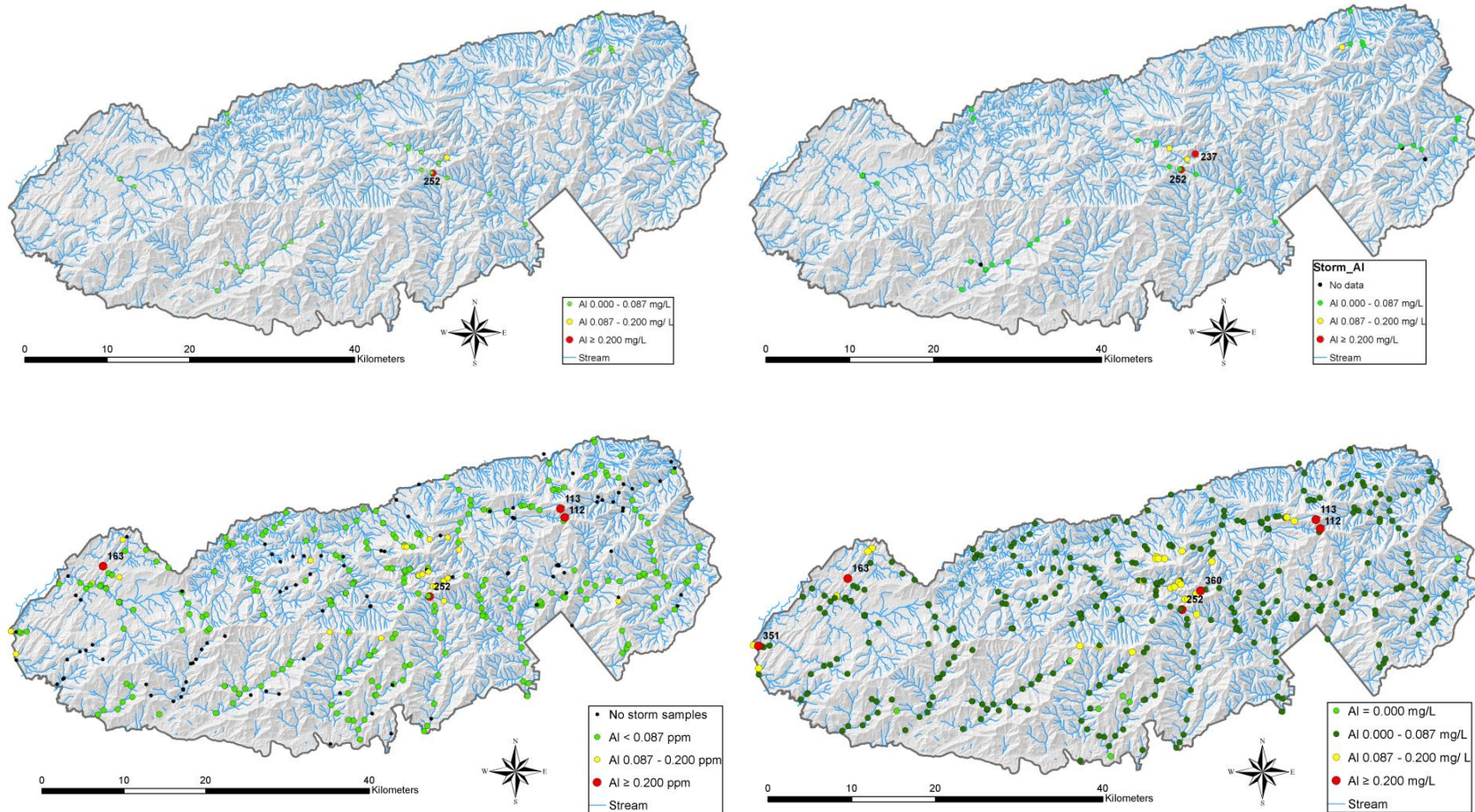


Figure 16. Median aluminum concentrations (mg L⁻¹) during baseflow (left) and stormflow (right) for the 43 currently monitored stream survey sites (upper) and 387 historical sites (lower) in GRSM from 1993-2009. Aluminum concentrations are estimates computed by a multiple regression model using [H⁺] and [SO₄²⁻] as predictors (Section 2.4.1).

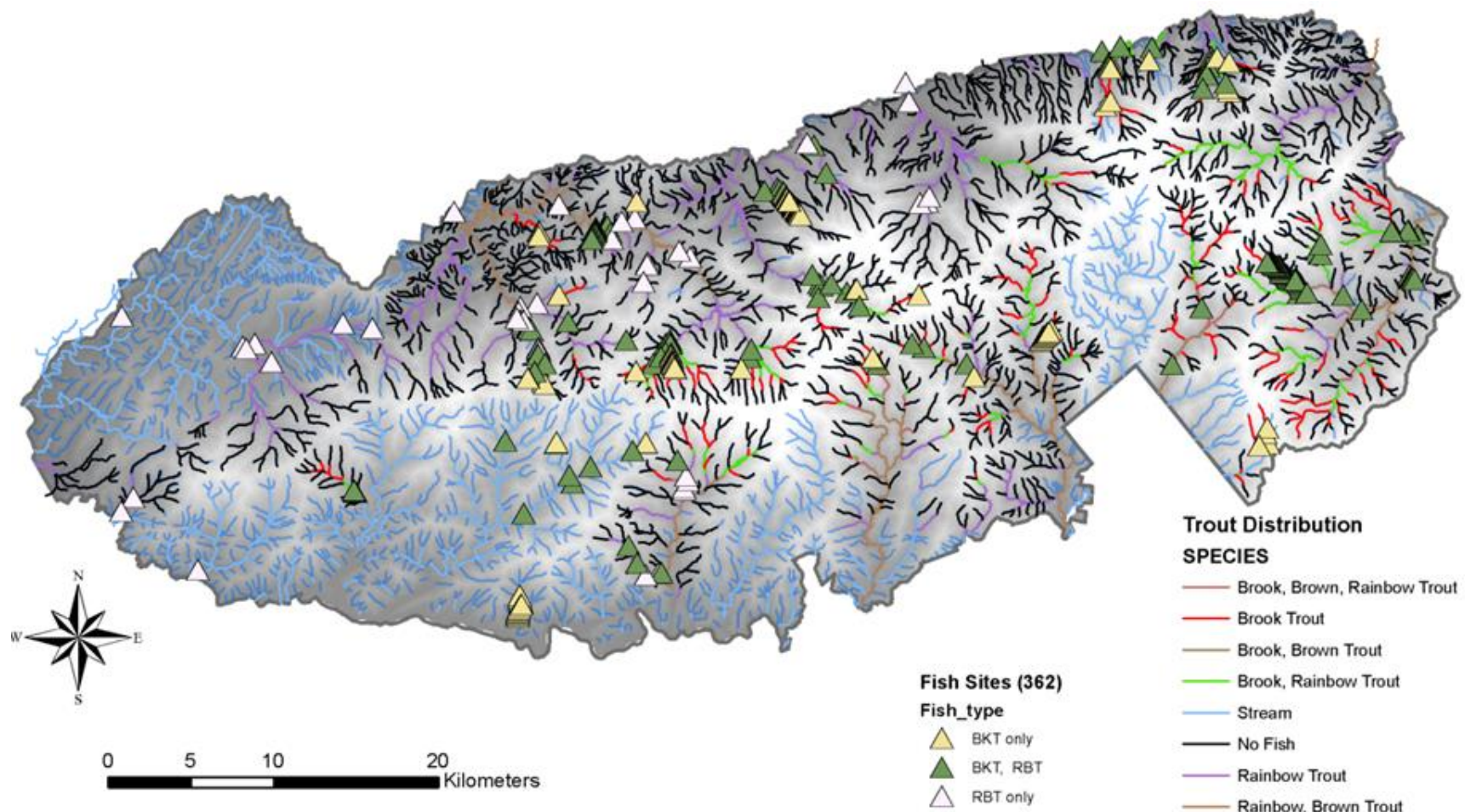


Figure 17. Distribution of brook and rainbow trout in GRSM streams as observed from presence/absence stream surveys (1994-2000) shown as lines and survey sites shown as points (1993-2009). Stream = not surveyed.

Table 9. Ranges of pH and chemical concentrations based on stream survey data for collocated water quality and fish sites from 1993 to 2009 (sites from Abrams Creek were excluded). Ranges summarized for sites with brook trout and rainbow trout occupancy. Chemical concentrations were in $\mu\text{eq L}^{-1}$, except pH in standard pH units and Al in mg L^{-1} . A zero value indicated an analytical instrument “non-detect” concentration.

		pH	ANC	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BCS	Al
Stream Range		5.0-7.2	-20-250	0-45	0-60	0-190	0-65	0-24	10-100	20-200	-20-300	0-0.13
Brook Trout	YOY	5.5-6.8	0-90			0-70	25-50	6-16	10-45	20-150	0-100	0-0.09
	ADT	5.5-6.8	0-90			0-70	20-45	6-16	10-45	20-150	0-100	0-0.09
Rainbow Trout	YOY	5.8-7.2	0-250		0-25		20-65	6-18			0-250	0-0.07
	ADT	5.8-7.2	0-250		0-25						0-250	0-0.13

stream survey sites were classified as having water quality not capable of supporting trout, capable of supporting brook trout only, rainbow trout only, or supporting sympatric trout populations.

The majority of stream survey sites were predicted to support both brook and rainbow trout based on water quality conditions (Fig. 18). In the upper watershed streams where only brook trout occur but water quality is sufficient for rainbow trout as well, it is likely that physical habitat governs trout distribution. Conversely in the lower watershed rivers and streams where only rainbow trout occur but water quality is sufficient for brook trout too, it is likely that interspecific competition plays a role (Larson and Moore 1985, Larson et al. 1995). Allopatric rainbow trout populations were predicted only among some lower elevation rivers and streams, and rarely predicted based on water quality conditions.

From a toxicological perspective, this analysis located stream survey sites in mid-elevations of watersheds where water quality predicts “no trout,” and sites were not occupied by either brook and/or rainbow trout (Fig. 18). These “no fish” sites should be considered as streams of potential concern, being potentially impacted by acidification. These streams include: Buck Prong, Ramsey Prong, Shutts Prong, Trillium Branch, Raven Fork (unnamed tributary on Breakneck Ridge), Alum Cave Creek, and upper Walker Camp Prong.

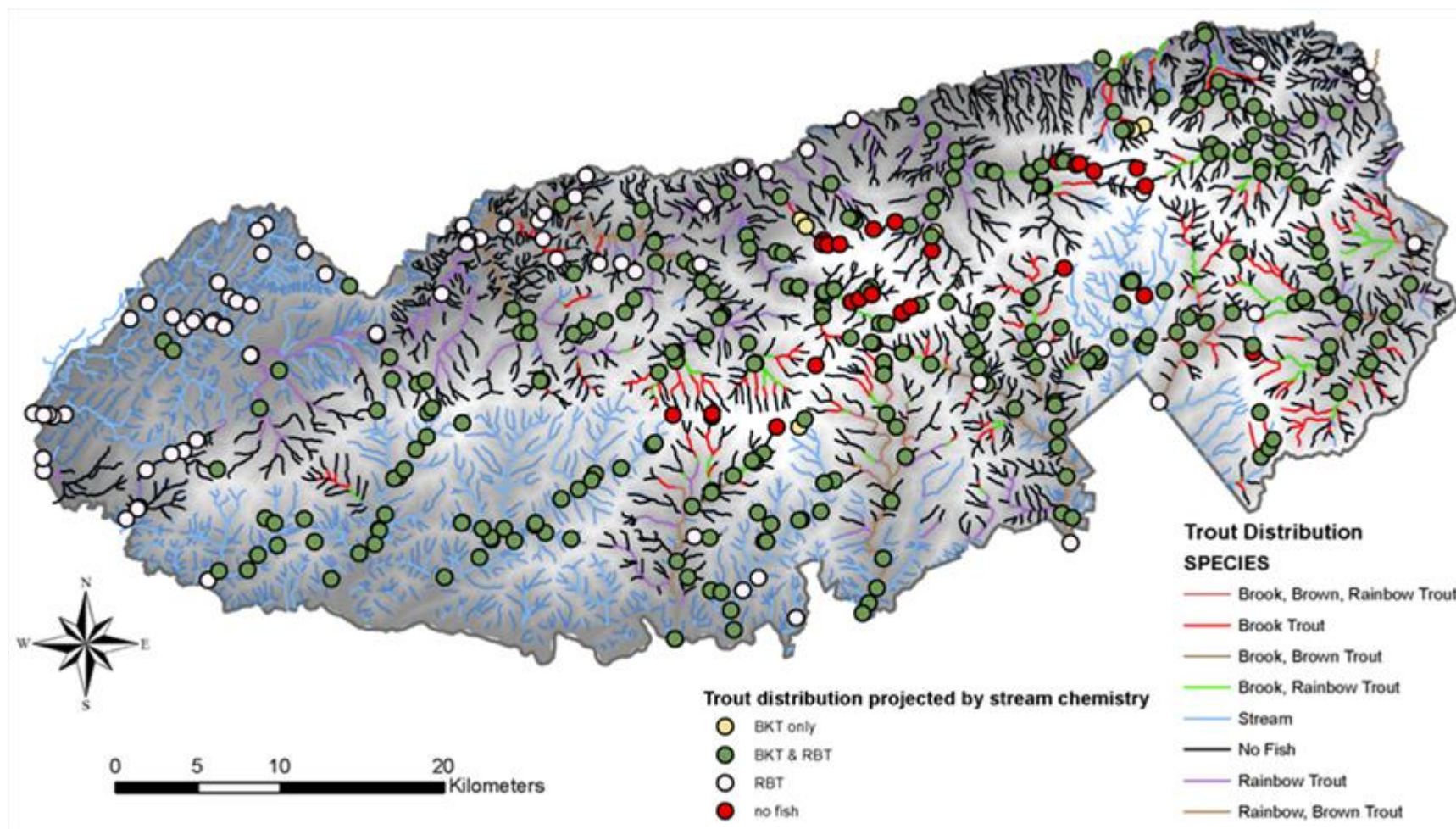


Figure 18. Distribution of brook and rainbow trout in GRSM streams based on predictions from water quality monitoring data (1993 to 2009) and pH and chemical concentration ranges per fish occurrences (Table 9).

5.0 Temporal Trend Analysis: Water Quality and Biotic Metrics

5.1 Methods: Temporal Trend Analysis

Temporal trends among water chemistry parameters and biotic metrics for trout and benthic macroinvertebrates were conducted using linear regression models. In the models, the dependent (y) variables were chemical measurements and biotic metrics for brook and rainbow trout and macroinvertebrates. The independent (x) variable was Julian date (year) where the slope of a significant model represented an increasing or decreasing trend over time. Significance levels for chemical concentrations were $p < 0.05$ and for biotic metrics $p < 0.10$. The significance level for biotic metrics was less than for chemical concentrations because of the higher variance and less statistical degrees of freedom for ecological data.

Temporal trend analyses require data monitoring on a regular sampling frequency and accrual of sufficient data to be statistically viable. Although water quality monitoring data included a total of 387 stream survey sites, only 295 sites were sampled for one to three years between 1993 and 1996. Fish and macroinvertebrate temporal data was more limited than the water quality data. Notes on methods and data interpretation for the time trend analyses include the following:

- Water chemistry parameters for 92 stream survey sites with data between 1993 and 2009 include: pH, ANC, conductivity, Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Al, and base cations. Mg^{2+} and Ca^{2+} were excluded between 1993 and 1998 due to differences in analytical instrumentation used in the laboratory.
- Fish metrics were collected from non-collocated stream survey sites between 1990 and 2009; macroinvertebrates were collected from non-collocated sites between 1990 and 2003.
- Results were organized by water quality sites that were not collocated with fish and macroinvertebrate sites ($N = 52$), and by those that were collocated ($N = 40$) (Tables 10, 11).
- Water chemistry parameters spatially-assessed temporal trends for the 43 currently-monitored stream survey sites, and focused on key acidification parameters such as pH, ANC, NO_3^- , SO_4^{2-} , Ca^{2+} , and Al.

Also, stream chemistry in the Abrams Creek watershed was greatly influenced by the carbonaceous geology where pH, ANC, and base cation levels were much greater than streams located in sandstone geology. Because of the severe statistical leverage caused by the Abrams Creek survey sites, three survey sites were removed from the temporal trend analyses. They were site ID numbers 156 (at ranger station), 174 (below Cades Cove), and 489 (300 m below trailhead bridge).

5.2 Water Quality Temporal Trends

Trends in stream pH were examined, for data between 1993-1995 to 2003 among non-collocated sites with biotic metric data, and for the collocated sites. Stream pH units for eight of the 52 non-collocated sites increased significantly at small annual increments in the range of 0.0 to 0.03 units (Table 10). Of the 40 collocated sites, pH for 14 sites increased in the range of 0.01 to 0.15 units yr^{-1} (Table 11). Two stream sites were observed to decrease in pH over this monitoring

time period [Porters Creek (site 43), lower Rock Creek (site 4)], declining at an annual rate of 0.03 pH units each. Both of these sites were observed to decline in ANC, measured at an annual rate of -1.57 and -3.22 $\mu\text{eq L}^{-1}$, respectively. Three sites were observed with no pH trends, but did exhibit declines in ANC

Table 10. Time trends of stream chemistry for non-collocated sites for the period 1993 to 2009. Periods of record differ per site and are defined in Appendix 1. Units: $\mu\text{eq L}^{-1} \text{yr}^{-1}$ except pH as pH unit yr^{-1} , conductivity as $\mu\text{S cm}^{-1} \text{yr}^{-1}$, and Al as $\text{mg L}^{-1} \text{yr}^{-1}$. Significance level = $p < 0.05$.

Site ID	N	pH	ANC	Cond	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	* Mg ²⁺	* Ca ²⁺	Al
3	44				0.0015	-0.0028	-0.0026				-0.0021	-0.0147			
14	39											-0.0092			
23	103	0.022		0.213	-0.0010						0.0030		0.0063	0.0083	
24	80	0.037				0.0009						-0.0037			-0.037
34	83	0.037				0.0023	0.0015			0.0002	0.0005				
43	62	-0.032	-1.573		0.0027					0.0010				0.0114	
45	49				0.0017			0.0020		0.0007					
46	46							0.0019				-0.0050			
49	46				0.0015									-0.0163	
50	35											-0.0071			
52	46									0.0011		-0.0050			
66	105	0.037		0.165		0.0014		0.0006		0.0003			0.0022	0.0066	
73	85			0.120		0.0010								0.0071	
74	83	0.021		0.225	0.0011			0.0012						0.0115	
103	53						-0.0030				-0.0009	-0.0090			
104	45				0.0024		-0.0035					-0.0106			
106	43				0.0014							-0.0056			
115	31									0.0018					
127	42											-0.0074			
138	46	0.031				-0.0031									
144	76					0.0011						-0.0025			-0.037
183	39												0.0030	0.0118	
184	44	0.019		-0.249		-0.0025	-0.0024				-0.0012	-0.0082			
193	62				0.0028					0.0010		-0.0058			
194	44						-0.0014					-0.0062			
195	33			-0.183		-0.0008	0.0005						0.0019		
200	44				0.0028	0.0022		0.0033		0.0015		-0.0052			
201	38					-0.0033				0.0009		-0.0052			
209	45							0.0022				-0.0021	0.0030		
210	47				0.0018			0.0016				-0.0083	0.0030		
213	46				0.0018							-0.0045			
218	52		-2.129			0.0079	-0.0042								
219	39				0.0039	-0.0081		0.0038			0.0020		0.0035		
220	38				0.0025			0.0023					0.0060		
233	78			0.212				0.0006						0.0092	
234	66						0.0009						0.0008		
237	97					0.0017								0.0038	
252	79							-0.0014						0.0108	
253	79						0.0083						0.0030	0.0058	
266	35							0.0031		0.0010					
268	76						0.0013					-0.0023			-0.037
290	23					-0.0146									
291	42					-0.0040		0.0026				-0.0066			
293	101	0.037		0.089		0.0017	0.0006					-0.0023	0.0013	0.0022	
310	51				-0.0016										
311	45					0.0012				0.0007		-0.0033			
472	29											-0.0071	0.0043	0.0082	
473	32							0.0021							
474	38						-0.0018					-0.0109			
475	31						-0.0016	0.0037				-0.0095			
480	40						0.0010					-0.0033	0.0017	0.0023	
482	36						0.0015			0.0006		-0.0036			
483	38						0.0022					-0.0040			

* Denotes Mg²⁺ and Ca²⁺ data from 1999 to 2009; data prior to 1999 did not meet QA/QC criteria.

Table 11. Significant trends of stream chemistry ($p < 0.05$), and trout and benthic macroinvertebrate metrics determined by using linear regression ($p < 0.1$). The numbers in the table give the trend rate per year from 1993 to 2009, except for Mg^{2+} and Ca^{2+} , which are based on data collected since 1999. Fish units for density (Dens) = fish/100 m²/yr and biomass (Biom) = kg/ha/yr. Chemistry units: $\mu eq L^{-1} yr^{-1}$ except pH as pH unit yr⁻¹, and Al as mg L⁻¹ yr⁻¹.

Trout														Chemistry survey														Macroinvertebrates							
	BKT						RBT																												
Site ID	N	YOY Dens	Adult Dens	YOY Biom	Adult Biom	YOY K	Adult K	N	YOY Dens	Adult Dens	YOY Biom	Adult Biom	YOY K	Adult K	Site ID	N	pH	ANC	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Al	Site ID	N	Biotic index	EPT richness	EPT abund, %	Taxa richness	Taxa abundance	
ICC-2	17				-0.681			7		0.045		0.171			1	43			0.3750									ICIC01	1						
ROC-2	13	-0.263		-0.108	-0.356		0.013	12	-0.035		-0.003			0.009	4	43	-0.030	-3.215		1.103	0.860	-1.060						CBRC01	5				-0.071		
CAN-1								9							47	81				-0.702	-0.710							MPCA01	2						
RPR-5	18					0.021	0.006	2							71	84				-0.390	0.401			0.159	0.446			WPRP01	11						
ICC-3N	15			0.085		0.014									107	62		-0.837	1.134			0.727	0.792				ICIC02	1							
ROC-7	20						0.006	1							137	84												CBRC02	11						
LOB-0	12						0.010	12	-0.205	-0.730	-0.070			0.012	143	77		-0.269								0.008	CTLB01	12							
LCT-1M	1							1							148	70	0.017	-0.363	0.265					0.366			CTLC01	1							
ABC-1								7							156	40				-0.569			-0.414				ABAB01	9				-0.017			
THD-C1								6	1.159					0.016	190	39		0.686		-0.502	0.730					2.120		MLTH02	1						
SAM-6	14					0.018	0.004	5						-0.023	191	41			-0.816								MLSA02	8							
STK-1	15					0.012	0.007	10							192	45			0.953			0.985			1.264		MLST01	7							
SIL-1	14														214	50				-0.526		0.891	0.263				ELSI01	11							
ACB-1	2							2							215	48					1.339		0.239	1.926				ELAS01	3						
HAZ-2N	2							2							224	10	0.145											HZHZ03	9						
BEF-1	7							7					0.053		251	93	0.019	0.700					0.134			-0.005	OWBF04	1							
BEF-0	1							1							270	34	0.061			-1.041	1.233					-1.141	-0.006	OWBF01	1						
FLT-1	17					0.013									336	41												BNFL01	10						
BUN-1	19		1.000												337	45	0.025					0.815						BNBU01	11	-0.057					
BUN-2	20		1.113		1.204	0.010									337	45	0.025					0.815						BNBU02	8		1.892				
HAZ-1	1							5			-2.447	0.031			484	38		-0.509					0.240				HZHZ02	9							
ABC-2								9	1.250		1.207	-0.006	-0.003		489	63	0.025	-0.807	0.229	0.705	-0.553					-0.007	ABAB02	9	-0.043						
CAT-4	10			0.011			0.010	16						0.003	493	62	0.019	-0.510	0.466	0.232	-0.744					-0.010	CTPC02	10							
LRV-0								3	-0.051	-0.163		-1.406			13	80				0.319															
LRV-1								14							20	46			0.622			0.689	0.306												
LRV-2								13							34	37				-0.546															
COS-2	15						0.004								114	69	0.010	-0.689	-0.549	0.360	0.581														
BEC-1	17	0.455	0.366	0.126	0.697			17	-0.521	-0.433	-0.080	-1.316		0.003	142	75	0.001	-0.365	0.166																
CAT-1	7							15		-0.206		-1.110	-0.004		147	93	0.007		0.338	0.180			0.198	0.352	0.922	-0.007									
CAT-2	2							15	-0.233	-0.227		-0.646	0.003		149	69	0.014	-0.238	0.520					0.288		-0.051									
CAT-3	3							15		-0.251		-0.814	-0.007		150	35																			
MIL-1								9		-0.293		-0.952	0.008	0.007	173	83	0.017	8.538	-0.282	0.493							-0.010								
ABC-3								10	1.123		0.551				174	80		-0.329	0.151																
ANC-1								9	-0.506		-0.379				186	61		0.701		-0.855			0.235	1.851	2.985										
HAZ-3	12														221	38										0.611									
SAM-1	7		0.441				-0.019	8		-1.274		-4.850			472	29								1.568	29.999										
WAL-1N	7				-0.543			6							485	38			0.396																
MIL-2								10		-0.281		-0.971			488	70			0.615	0.312				0.425	0.847										
															479	40			0.414																
															492	63	0.025	-0.807	0.229	0.705	-0.553			0.669	1.020	-0.007	HZHZ01	9							
																												CBCM01	1						
ALC-1	3							2																				WPAL01	2						
BRC-18	2							1																				FOBC01	2						
DEF-1																												HZDF01	5	-0.101					
DUN-4	1																											DNDN01	1						
GBC-1	1							1																				GRGR01	1						
LBTRA-1	7		1.795		3.161			2																				CTTA02	2						
LOB-24	7				1.880			3		-1.212		-4.439	0.128															CTLB02	2						
LOB-34	8							4																				CTLB03	10						
STR-2	11							11		-0.178		-0.777																SRSF02	1						
TAY-2	1																											BRTA01	11		-0.730				

[Indian Camp below Albright Grove (site 107), Cosby Creek (site 114), Silers Bald spring (site 218)]. Two sites, Mill Creek above Abrams Creek (site 173), and Beech Flats above US 441 (site 251), were observed with an ANC increase of 0.70 and 8.52 $\mu\text{eq L}^{-1} \text{yr}^{-1}$, respectively. Of the 92 stream survey sites assessed, 67 sites were observed to have no time trends for pH and ANC. Of the 43 currently monitored streams, sites with degrading acidification trends were located in the Cosby-Rock Creek drainages (Fig. 19). Most stream sites at higher elevations were observed with no trends or slightly improving from acidification conditions.

Collectively across GRSM, acid anions (Cl^- , SO_4^{2-} , and NO_3^-) showed both increasing and decreasing annual concentrations over time among the 92 sites (Tables 10, 11). Chloride increased at 19 stream survey sites ranging from 0.38 to 1.41 $\mu\text{eq L}^{-1} \text{yr}^{-1}$, and decreased at 13 sites ranging from -0.24 to -0.81 $\mu\text{eq L}^{-1} \text{yr}^{-1}$. Sulfate increased at 18 stream survey sites ranging from 0.17 to 3.03 $\mu\text{eq L}^{-1}$, and decreased at 14 sites ranging from -0.49 to -1.55 $\mu\text{eq L}^{-1} \text{yr}^{-1}$. Nitrate increased at 25 stream survey sites ranging from 0.15 to 2.88 $\mu\text{eq L}^{-1} \text{yr}^{-1}$, and decreased at 12 sites ranging from -0.29 to -5.32 $\mu\text{eq L}^{-1} \text{yr}^{-1}$. Annual increases in stream nitrate concentrations appeared to dominate over decreasing trends among the 92 sites monitored; however, 56 stream sites observed no NO_3^- time trends. Of the 43 currently monitored streams, two sites with the greatest annual increases in SO_4^{2-} concentrations were located at high-elevation survey sites, whereas increasing NO_3^- concentration rates were located at the lowest elevation sites (Fig. 20). These results indicate that watershed characteristics have a dominant control over water quality time trends and the period of time that recovery will occur from acidic deposition.

Base cations (Ca^{2+} , Mg^{2+} , K^+ , and Na^+) generally increased over the analysis periods (Tables 10, 11). Calcium exhibited the greatest rates of increase among the base cations, and many of the stream survey sites increased over 2 $\mu\text{eq L}^{-1} \text{yr}^{-1}$. Among the 92 stream survey sites, 20 sites were observed with increasing Ca^{2+} time trends, and only site 270 (Beech Flats at Kephart footbridge) was observed with a decreasing trend. Similarly, 23 sites were observed with increasing Mg^{2+} time trends ranging from 0.29 to 2.31 $\mu\text{eq L}^{-1} \text{yr}^{-1}$, and no sites were observed with decreasing trends. Additionally, stream survey sites with observed increasing time trends for K^+ and Na^+ included 21 and 22 sites, respectively. In general, these results suggest that some watersheds may be experiencing base cation export. Only one site showed a decreasing trend for K^+ , and four sites for Na^+ . Of the 43 currently monitored stream sites, Ca^{2+} increased over time in the West Prong of the Little Pigeon River along US 441, where limestone chat is used for road traction during winter months (Fig. 21).

Dissolved aluminum was the one metal assessed for time trends because of its potential toxicity to biota (Section 4.1). Of the 92 stream survey sites assessed, 10 sites were observed with decreasing annual concentration rates in the range of -0.005 to -0.051 mg L^{-1} (Tables 10, 11). Only one site was observed with an increasing aluminum time trend [Lost Bottom Creek at Cataloochee Creek (site 143)], at a rate of 0.008 $\text{mg L}^{-1} \text{yr}^{-1}$. Sites with decreasing annual Al concentration trends were distributed across GRSM as assessed per the current water quality monitoring sites, which included the Cataloochee Creek and Oconaluftee River drainages (Fig. 21).

5.3 Biotic Metrics Temporal Trends

Of the 298 fish survey sites, 56 had surveys with eight or more years of data for the period 1990 to 2009 (Appendix 11). The macroinvertebrate dataset contained 13 survey sites with eight or more annual collections for the period 1990 to 2009 (Table 11). Because most biotic survey sites had less than eight surveys, many of which only had one or two data points, temporal trend analyses were

limited for these datasets. Significant temporal trends for trout at some survey sites ($p < 0.1$) included increased adult brook trout density (fish/100 m²) and biomass (kg/ha) corresponding with decreased adult rainbow trout density and biomass (Appendix 11). Adult brook trout density and/or biomass increased over time in 27 sites, and decreased in three sites. Adult rainbow trout density and/or biomass decreased at 16 sites, and increased in only three sites. Between brook and rainbow trout, these opposing temporal trends co-occurred in only six sites [Beech Creek (BEC-2), Lost Bottom Creek (LOB-8, LOB-11, LOB-14, LOB-15), Sams Creek (SAM-3)]. The condition factor K for adult brook trout was observed to significantly decline in four Lost Bottom Creek sites at very small annual rates of change (-0.0001). Although a temporal trend analysis on biotic metrics provided some general information of GRSM trout populations, it did not identify relationships with water quality. Identifying these relationships requires examining temporal trend analyses at collocated stream survey sites (Section 5.4).

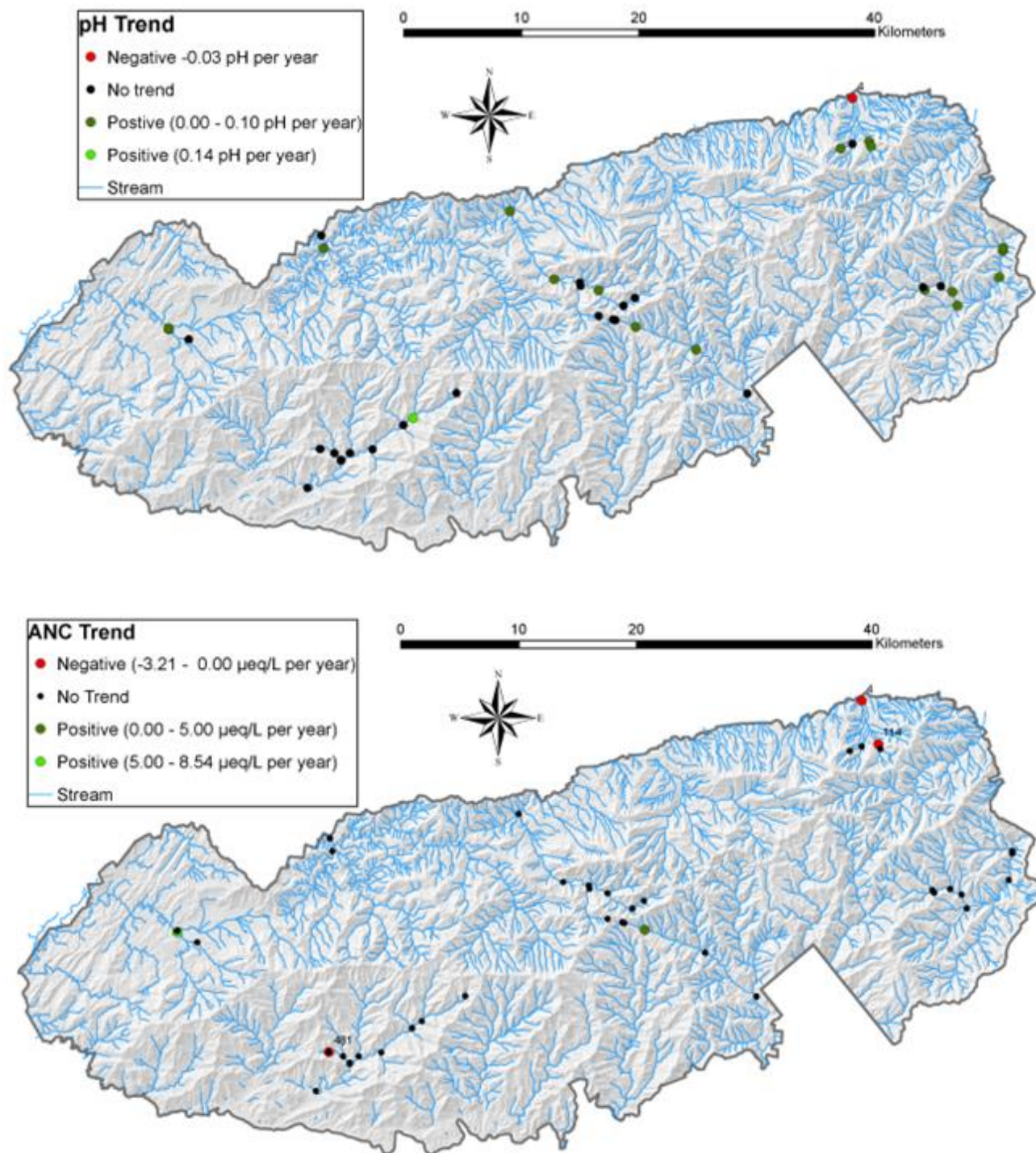


Figure 19. Temporal trends in stream pH and ANC between 1993 and 2009 for the 43 stream survey sites currently monitored.

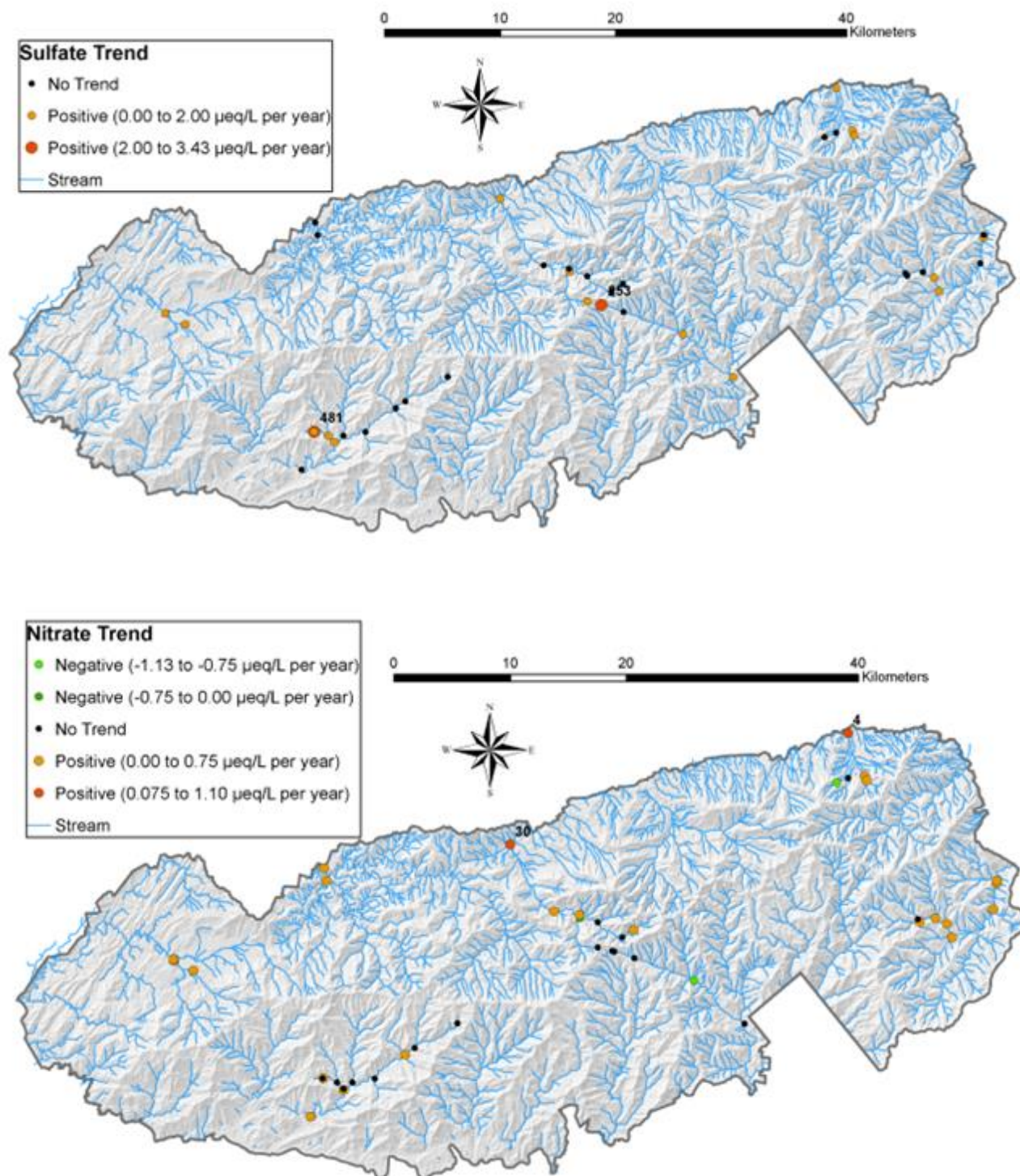


Figure 20. Temporal trends in stream sulfate and nitrate concentrations between 1993 and 2009 for the 43 stream survey sites currently monitored.

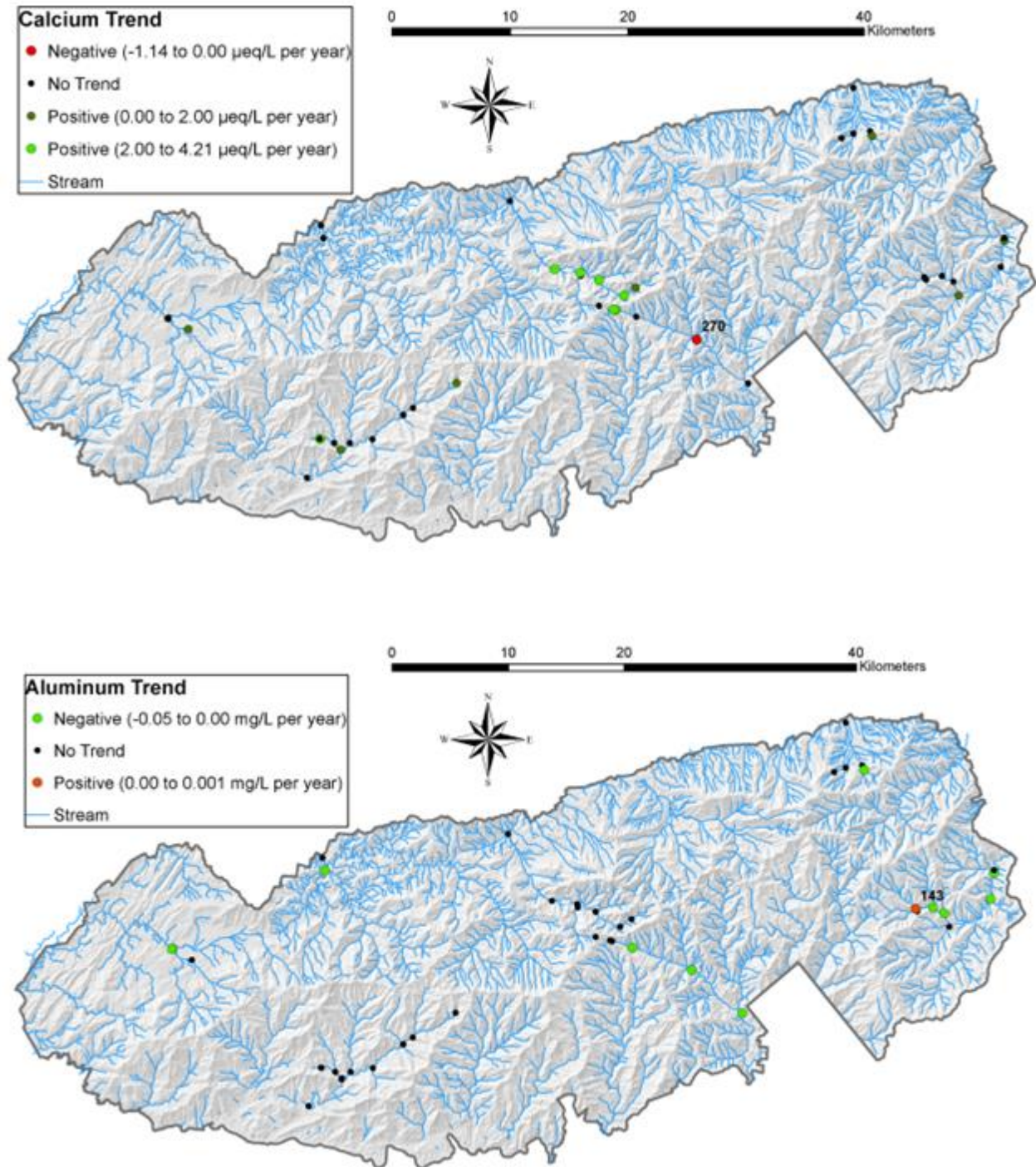


Figure 21. Temporal trends in stream calcium and aluminum concentrations between 1993 and 2009 for the 43 stream survey sites currently monitored.

5.4 Temporal Trends among Water Quality and Biotic Metrics

Both increases and decreases in brook and rainbow trout metrics over time among the collocated stream survey sites, and their associations with water quality, appear to be specific to individual watersheds (Table 11). Because water quality conditions in each watershed vary across GRSM, an analysis of spatial relationships among water quality, fish, and macroinvertebrates was conducted. Significant findings from this trend analysis are summarized below.

Annual brook trout biomass (kg/ha) declined at two fish survey sites [Rock Creek (ROC-2), Walker Creek (WAL-IN)]. The Rock Creek site also showed a decline in YOY rainbow trout density and biomass, and EPT percent abundance. Both sites had an increase in annual sulfate concentration, but only Rock Creek had a decrease in annual pH and ANC, and an increase in nitrate. Rock Creek appears to be negatively impacted by a worsening stream acidification condition.

Annual adult brook trout density increased at four fish survey sites [Bunches Creek (BUN-1, BUN-2), Beech Creek (BEC-1), Sams Creek (SAM-1)]. All sites except Sams Creek had a significant increase in annual stream pH (Table 11). The annual increase in stream pH at the Beech Creek site was small ($+0.001$ units yr^{-1}), likely due to the decreased annual chloride concentration observed at -0.365 $\mu\text{eq L}^{-1} \text{yr}^{-1}$. Sodium ions have been reported as favorable to trout, and at the two Bunches Creek sites, annual sodium concentrations increased at 0.815 $\mu\text{eq L}^{-1} \text{yr}^{-1}$. YOY brook trout biomass increased at Palmer Creek (CAT-4) and Indian Camp Prong (INCC-3N), where pH increased at Palmer Creek but not at Indian Camp Prong.

Adult rainbow trout density and biomass declined at 10 stream survey sites, but no patterns with water chemistry were observed. Three additional sites are listed where rainbow trout removals have occurred (Table 11). The 10 sites were as follows: unnamed tributary to Little River (LRV-0), Beech Creek (BEC-1), Cataloochee Creek (CAT-1, CAT-2, CAT-3), Mill Creek (MIL-1, MIL-2), Lost Bottom (LOB-24), Sams Creek (SAM-1), and Straight Fork (STR-2). Six of the 10 sites had an increase in annual stream pH, which was counter to an effect by acidification. Seven of the 10 sites had a significant increase in annual nitrate concentration, and it appears that stream acidification was buffered by an increase in base cation concentration. In general, annual declines in rainbow trout metrics among collocated water quality sites do not appear to be due to stream acidification.

6.0 Spatial Variation of Water Quality, Fish, and Macroinvertebrates

6.1 Elevation Trends in Water Quality and Biotic Metrics

In the Appalachian mountain region, changes in stream chemistry have been shown to occur along an elevation gradient (Gbondo-Tugbawa and Driscoll 2002, Sullivan et al. 2007, Robinson et al. 2008). In general, stream acidification increases with increasing stream elevation, where higher elevations are associated with greater acid deposition (Weathers et al. 2006). Once acid pollutants enter watersheds via atmospheric deposition, vegetation, soils, and surficial geology influence their fate and transport to streams (Driscoll et al. 2001, Deyton et al. 2009, Neff et al. 2013). Brook trout are known to occupy smaller headwater streams in the Appalachian region, and rainbow trout commonly occupy larger streams (Larson and Moore 1985, Hyer et al. 1995, Webb et al. 2004, Kocovsky and Carline 2005). Although not specifically referenced by elevation, macroinvertebrate community composition is known to change from headwaters to lower elevation, larger streams (Vannote et al. 1980, Yates and Bailey 2010).

6.1.1 Methods: Elevation Trends

Linear regression models were developed to characterize elevation gradients for water chemistry, and trout and macroinvertebrate metrics. Chemical parameters and biotic metrics were the dependent variables, while elevation was the independent variable. Regression line slopes represent the unit change (+/-) for each 1000 ft (305 m) in elevation, where $p < 0.05$ was considered a significant model.

A detailed analysis was conducted with sulfate concentrations because of its soil geochemical interactions and potential dominant role in episodic stream acidification. In this analysis, water chemistry data were grouped into elevation bands [< 1000 ft (305 m); 1000-2000 ft (305-609 m); 2001-3000 ft (610-914 m); 3001-4000 ft (915-1219 m); 4001-5000 ft (1220-1524 m); and > 5000 ft (1524 m)] and different monitoring periods (1993-2009; 1993-2003; 1993-1996; and 1993-1995). In this analysis, a Tukey HSD means separation method was used to test whether significant differences occurred among the elevation bands for each monitoring period. Statistical significance was considered for a p -value < 0.05 . A qualitative assessment was conducted for temporal trends among monitoring periods for common elevation bands.

6.1.2 Elevation Trends with Water Chemistry

Based on the complete 1993-2009 dataset, the basic trend of increased acidification with increased elevation was observed in GRSM (Table 12). Stream pH and ANC significantly decreased at -0.32 pH units and $-35.73 \mu\text{eq L}^{-1}$ respectively, per 1000-ft (305 m) elevation gain. Sulfate exhibited a declining trend with elevation gain, although its slope was insignificant, and nitrate exhibited a significant increase with elevation gain. Conductivity, chlorine, and base cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) exhibited significant decreases with elevation gain. From the GRSM park-wide dataset, results suggest that increased baseflow-dominated stream acidification from lower to higher elevations occurs from decreasing base cations, which corresponds with increasing nitrate.

Stream sources of base cations are from atmospheric deposition and chemical weathering of soils and base rock. In general, base cation concentrations increase in larger streams and rivers because greater watershed area and lower elevation lead to more groundwater contributions

(Mulholland 1993, McKenna 2007, Zimmerman 2011). In headwater areas, soil adsorption may be dominant in retaining

Table 12. Elevation trends of median chemical concentrations, and macroinvertebrate and trout metrics in GRSM streams from 1993 to 2009. Chemical concentrations are all in $\mu\text{eq L}^{-1}$, except pH is in pH units, and conductivity (Cond) is in $\mu\text{S cm}^{-1}$. Note, median ammonia (NH_4^+) concentrations were near zero. Macroinvertebrate richness (species numbers) and abundance (individual numbers) are expressed per collection site. NCBI is a dimensionless index. Trout density (Den) and biomass (Biom) are in fish/100 m^2 and kg/ha, respectively. Slopes are unit per 1000 ft (305 m). Significance level is p-value < 0.05 .

Chemistry (N = 385)			Macroinvertebrates (N = 113)			Trout	BKT (N = 240)		RBT (N= 204)	
	Slope	p-value		Slope	p-value		Slope	p-value	Slope	p-value
pH	-0.32	<0.01	NCBI	-0.22	<0.01	YOY_Den	2.23	<0.01	-1.02	<0.01
ANC	-35.73	<0.01	EPT Richness	-1.55	0.02	ADT_Den	5.03	<0.01	-0.39	0.12
Cond	-1.70	<0.01	EPT Abundance	0.02	0.05	YOY_Biom	0.45	<0.01	-0.57	<0.01
Cl ⁻	-0.33	0.03	Taxa Richness	-5.68	<0.01	ADT_Biom	9.12	<0.01	-3.01	<0.01
NO ₃ ⁻	8.42	<0.01	Taxa Abundance	-31.26	0.04	YOY_K	-0.03	<0.01	-0.03	0.02
SO ₄ ²⁻	-1.52	0.25	<u>Richness</u>			ADT_K	-0.02	<0.01	-0.02	<0.01
Na ⁺	-5.93	<0.01	Collector-Filterer	-1.10	<0.01					
K ⁺	-1.57	<0.01	Collector-Gatherer	-1.85	<0.01					
Mg ²⁺	-9.07	<0.01	Predator	-1.38	<0.01					
Ca ²⁺	-19.67	<0.01	Scraper	-1.23	<0.01					
			Shredder	0.04	0.85					
			<u>Abundance</u>							
			Collector-Filterer	-0.017	0.03					
			Collector-Gatherer	0.010	0.21					
			Predator	0.001	0.78					
			Scraper	-0.015	0.01					
			Shredder	0.019	0.03					

base cations from atmospheric deposition. Nitrate from atmospheric deposition is either taken up by forest vegetation or rapidly passed through soils to the streams. In the Appalachian region, more nitrate is deposited than what forests can uptake; therefore, it is exported to the streams, and this excess export is termed 'stage 2 forest nitrogen (N) saturation' (Williard et al. 1997, Eshleman et al. 1998, Mitchell 2001). Van Miegroet et al. (2001) explicitly reported the occurrence of stage 2 N saturation at the high-elevation Noland Divide research site. A longitudinal gradient of nitrate with decreasing concentrations from high-elevation headwaters to low-elevation streams is likely due to greater nitrate deposition at higher elevations, with stage 2 N saturation occurring in the headwater forest watersheds (Van Miegroet et al. 2001, Weathers et al. 2006), and rapid nitrate uptake by periphyton and biofilm in flowing stream water (Mulholland 2004). Two cautionary notes are suggested with this interpretation. First, this observation represented a general longitudinal profile trend for baseflow conditions mostly, and not specific to any watershed or stormflow stage. Deyton et al. (2009) found that the controlling chemical causes in episodic acidification varied by specific watershed and season (leaves on/off). Secondly, most of the data used in this analysis was from the period 1993 to 1995; therefore, this result could differ from a more recent monitoring effort focused on a longitudinal gradient study design. Baseflow and stormflow conditions would also need to be separated in the analysis.

Lack of a significant elevation trend with in-stream sulfate concentrations suggests that soil adsorption in the higher elevation headwaters plays a dominant role in affecting this water chemistry parameter during baseflow conditions. Weathers et al. (2006) reports greater sulfate deposition in the higher elevation areas in GRSM. However, sulfate was not found to be exported to streams in greater concentrations at the higher elevations, as interpreted from the results (Table 12). Neff (2010) examined source contributions of stream sulfate and found that atmospheric deposition was dominant over weathering of exposed Anakeesta rock in a park-wide analysis. The results also indicated that stream sulfate concentrations do not vary significantly from high to low elevation, and export from soils to streams is controlled by adsorption processes. Sulfate adsorption in soils at Noland Divide appears to be controlled by acid deposition as a function of throughfall concentrations, and ammonia, which is converted to nitrate by soil nitrification, then adds to soil acidity (Cai et al. 2010, 2012). Sulfate remains adsorbed to soil particles as long as soil water chemistry remains high in sulfate concentration and low in pH (Cai et al. 2011a).

Because depositional sulfate has been adsorbed in the higher elevation soils for years, one concern is the potential for rapid desorption of this stored sulfate if acidic deposition conditions change too rapidly. Cai et al. (2011a) reported that if soil water pH increases above approximately 6.0 and sulfate concentrations drop below $15 \mu\text{mol L}^{-1}$, sulfate desorption will dominate over adsorption. Because the elevation trends (Table 12) were for the entire data set, sulfate trends were further analyzed examining for differences by monitoring period (Table 13). Stream sulfate concentrations appeared to be greatest between 4000 ft (1219 m) and 5000 ft (1524 m) elevation. Concentrations above 5000 ft elevation were less than the 4000-5000 ft elevation band; however, sample sites were very small compared to the other elevation bands, which may have influenced the result. Sulfate concentrations within the 3000 (914 m)-4000 ft (1219 m) band appeared to be greater than lower elevation bands, but differences were generally not significant. Recent trends show that sulfate concentrations may be currently increasing within two elevation bands (3000-4000 ft and 4000-5000 ft). Because of the limited number of

data points, this interpretation is highly speculative but does draw attention to the need for further elevation-based water quality studies. Higher elevation

Table 13. Average stream sulfate concentrations ($\mu\text{eq L}^{-1}$) for six elevation bands, grouped by monitoring periods. Number of samples per group is in parentheses. Using the Tukey HSD method, significantly different concentrations ($p < 0.05$) within columns (monitoring periods) are represented by different letters.

Elevation band	Elevation (ft)	Average sulfate concentration (number of survey sites)			
		1993-2009	1993-2003	1993-1996	1993-1995
1	< 1,000	NA (0)	NA (0)	64.79 ^{ABC} (2)	NA (1)
2	1,000-2,000	43.63 ^{AB} (6)	35.81 ^A (10)	42.31 ^{AB} (24)	29.88 ^A (16)
3	2,000-3,000	31.25 ^B (10)	30.87 ^A (5)	26.43 ^C (31)	34.66 ^A (28)
4	3,000-4,000	62.28 ^{AB} (4)	41.91 ^A (9)	30.37 ^{BC} (39)	29.96 ^A (26)
5	4,000-5,000	119.80 ^A (6)	60.82 ^A (2)	55.27 ^A (13)	50.50 ^A (12)
6	> 5,000	NA (1)	NA (0)	34.27 ^{ABC} (3)	43.39 ^A (6)

streams would experience increased sulfate and prolonged acidification if soil desorption becomes a dominant geochemical watershed process.

6.1.3 Elevation Trends with Biotic Metrics

As would be expected from trout distributions in GRSM (Fig. 17), brook trout density and biomass increased with elevation, and rainbow trout decreased (Table 12), although this is more a function of prior extirpation than chemistry effects. The elevation trends were all statistically significant except for adult rainbow trout ($p < 0.05$). Condition factor K values for both brook and rainbow trout decreased with elevation. Toxicity literature suggests that brook trout are slightly more tolerant to stream acidification than rainbow trout (Appendix 10). Watershed distribution and abundance of brook and rainbow trout are a function of many factors, and cannot be explained by a single-metric trend line. However, more advanced statistics attempting to associate trout metrics with water quality conditions follow in Chapter 7.

Some macroinvertebrate metrics significantly decreased with increasing site elevation (Table 12). Taxa richness decreased by 5.68 species and abundance decreased by 31.26 individuals per 1000 ft (305 m) elevation gain for a standard collection effort. EPT's and some functional feeding groups (collector-filterers, collector-gatherers, predators, scrapers, shredders) also decreased with increasing elevation. EPT abundance showed no trend with elevation gain.

6.2 Eight-block Watershed Design: Water Quality and Biotic Metrics

6.2.1 Methods: Eight-block Watershed Design

The eight-block design of watersheds was based on the Neff (2010) study specifically examining watershed characteristics and their relation to water quality and brook trout populations in GRSM (Table 14). The study was termed for the classification of three basin characteristics, which were: 1) elevation [above and below 3200 ft (975 m)]; 2) basin area [above and below 3.86 mi^2 (10 km^2); and 3) percent watershed area with Anakeesta geology (above and below 10%). The basin factor cut-offs were based on research outcomes from Deyton et al. (2009). The study design was also motivated by the fact that these three watershed characteristics collectively represent 77% [611 mi^2 (1582 km^2)] of the total GRSM land area; therefore, they could be used

to effectively assess the potential severity of acidification over a large portion of GRSM. The original eight watersheds selected included: Newt Prong, Road Prong, Rock Creek, Lost Bottom Creek, Jakes Creek, Walker Camp Prong, Cosby Creek, and Palmer Creek (Fig. 22). Latitude and longitude of the watershed outlet locations are in Table 14.

Table 14. Basin characteristics of the eight-block design watersheds including elevation, basin area, and percent watershed area with Anakeesta geology (Neff 2010).

BASIN	Elevation (m)	Area (km²)	Anakeesta (km²)	Mean basin elevation (m)	Mean basin slope	Latitude	Longitude
Newt	Low (870)	Small (4.09)	Present (1.97)	1214	23.6°	35.633 N	83.587 W
Road	High (1090)	Small (8.6)	Present (1.75)	1529	30.0°	35.630 N	83.470 W
Rock	Low (630)	Small (3.63)	Absent (0)	1249	25.8°	35.761 N	83.210 W
Lost Bottom	High (1015)	Small (8.45)	Absent (0)	1423	26.4°	35.637 N	83.146 W
Jakes	Low (660)	Large (12.01)	Present (4.02)	1096	22.5°	35.654 N	83.582 W
Walker Camp	High (1165)	Large (10.73)	Present (8.15)	1523	28.3 °	35.629 N	83.451 W
Cosby	Low (610)	Large (17.51)	Absent (0)	1112	28.2°	35.763 N	83.211 W
Palmer	High (990)	Large (19.99)	Absent (0)	1380	25.8°	35.636 N	83.144 W
Eagle Rocks *	High (975)	Large (10.47)	Present (1.17)	1445	30.5°	35.690 N	83.320 W

* Stream data used in Neff et al. (2013), but not in this study's statistical analysis.

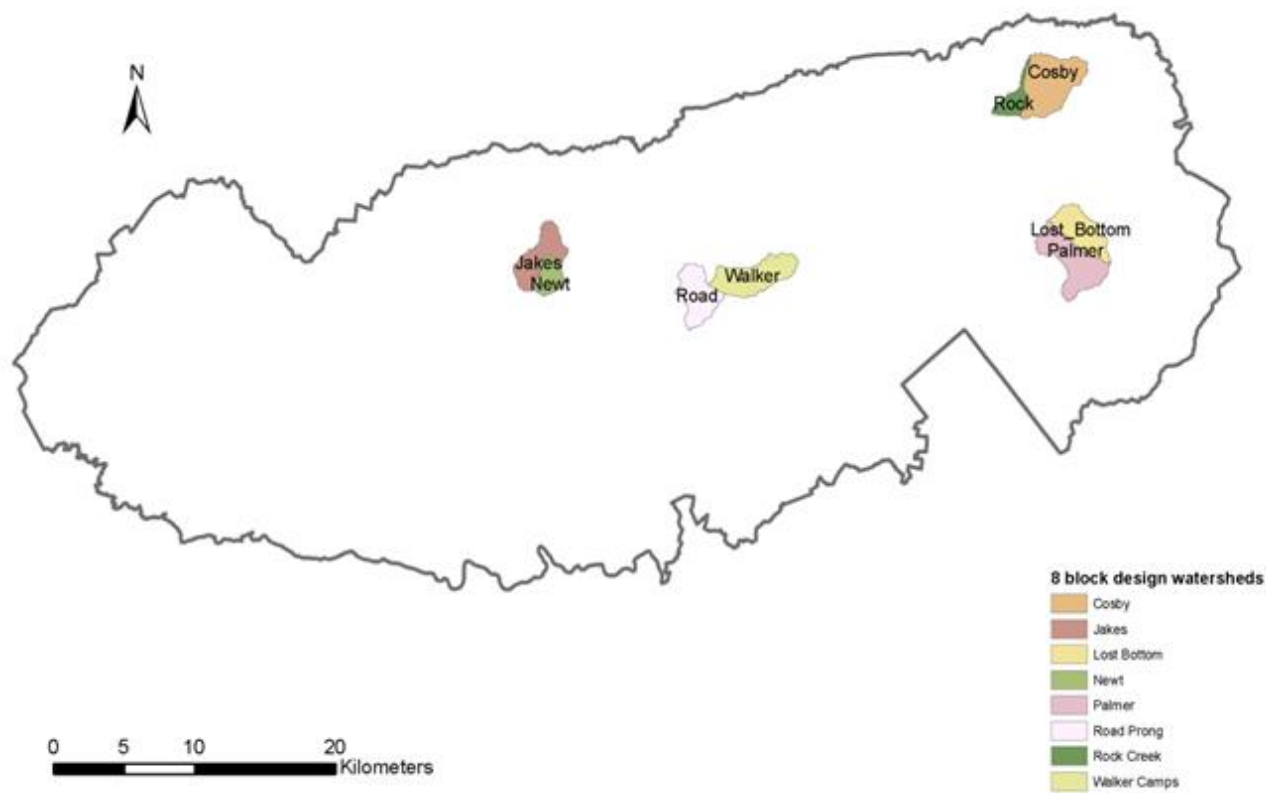


Figure 22. GRSM location map of the eight-block design watersheds used in this study.

In this report, statistical analyses of the eight-block design study watersheds focused on assessing differences in fish and macroinvertebrate metrics among the watersheds rather than water quality parameters because Neff et al. (2013) completed a thorough analysis of watershed characteristics (i.e., soil metrics, forest cover type, elevation, drainage area, geology) associated with water quality. In the Neff et al. (2013) study, Walker Camp Prong was replaced with Eagle Rocks Prong because of the use of dolomite chat on nearby roadways in winter, which affects water chemistry; therefore, Walker Camp Prong would not be representative of streams impacted by acid deposition. In our study, Walker Camp Prong was used in the statistical analysis because it accommodated fish populations whereas Eagle Rocks Prong did not. Statistical results in this study were interpreted with the understanding of the water quality effects from the dolomite chat.

Within the eight-block design study, there were seven fish survey sites excluding Newt Prong, and six macroinvertebrate sites excluding Newt Prong and Jakes Creek (Table 15). Statistical differences between two watersheds were examined by the student's *t* test. When three or more watersheds were examined, a Tukey HSD means separate test was used. Both statistical procedures were completed with JMP v.9.

6.2.2 Stream Chemistry

Relationships between stream chemistry, elevation, area, Anakeesta geology, soil properties, and dominant vegetation were evaluated to identify the influence of basin characteristics on baseflow and stormflow chemistry in the eight-block design streams. Statistical analyses were employed to determine differences between baseflow and stormflow chemistry, and relate basin-scale factors

governing local chemical processes to stream chemistry (Neff et al. 2013). Following precipitation events, stream pH was reduced and aluminum concentrations increased, while the response of ANC, nitrate, sulfate, and base cations varied. Several basin characteristics were highly correlated with each other, demonstrating the interrelatedness of topographic, geologic, soil, and vegetative parameters. These interrelated basin factors uniquely influenced the stream acidification response in these streams. Streams in higher elevation basins [> 3199 ft (975 m)] had significantly lower pH, ANC, sodium, and silicon, and higher nitrate concentrations during baseflows ($p < 0.05$). Streams in smaller basins [< 3.86 mi² (10 km²)] had significantly lower nitrate, sodium, magnesium, silicon,

Table 15. List of fish and macroinvertebrate survey sites located in the original eight-block design watersheds. Each large watershed has a small sub-watershed hierarchically embedded; small watersheds located inside their larger watershed unit are in parentheses. Site number descriptions are located in Appendices 8 and 9.

No.	Large watershed (small watershed)	Fish survey sites (sites in small watersheds)	Macroinvertebrate sites (sites in small watersheds)
1	Cosby Creek (Rock Creek)	COS-1A, TOM-2, TOM-1 (ROC-1, ROC-2, ROC-3, ROC-4, ROC-5, ROC-6, ROC-7)	CBCM01 (CBRC02, CBRC01)
2	Jakes Creek (Newt Prong)	JAK-1, JAK-2, (NWP-3)	None
3	Palmer Creek (Lost Bottom Creek)	BEC-1, BEC-2, (LOB-0 ~ LOB-34)	CTLB01, CTBE01 (CTTA02, CTLB02, CTLB03)
4	Walker Camp Prong (Road Prong)	KEB-1, WCP-2, (PRP-4, PRP-5)	WPWC01, WPAL01 (WPRP01)

and base cation concentrations. During stormflow, streams in basins with $> 10\%$ Anakeesta geology had significantly lower pH and sodium concentrations, and higher aluminum concentrations. However, baseflow chemistry was not influenced by the presence of Anakeesta geology. Chemical and physical soil characteristics and dominant overstory vegetation in basins were more strongly correlated with baseflow and stormflow chemical constituents than topographic and geologic basin factors. Increased proton (lower pH) and nitrate concentration occurred in streams with basins dominated by high-elevation forests, likely due to higher nitrification rates. This is consistent with what was observed with the elevation trends analysis in Section 6.1.

Of all the soil parameters, saturated soil hydraulic conductivity was most related to concentrations of stormflow constituents (Neff et al. 2013). Basins with higher average soil hydraulic conductivities were associated with lower stream pH, ANC, base cation concentrations, and higher aluminum, nitrate, and sulfate concentrations. In steep basins with higher soil hydraulic conductivities (Ksat), it is likely that interflow during storm events reduces the contact time with soils, limiting ion absorption and consequent buffering effect. Further analysis of interflow water chemistry would improve our understanding of transport loads and rates during storms.

6.2.3 Trout Metrics

Adult brook trout populations were significantly different among the eight-block design watersheds, except for the allopatric populations in large watersheds (Table 16). Large watersheds with allopatric brook trout populations are not common in GRSM (Fig. 17). Within the small watershed groups, adult brook trout density, biomass, and condition factor K were less in Rock Creek compared with Road Prong and Lost Bottom Creek. This result is interesting because Road Prong and Lost Bottom Creek are higher elevation streams which generally experience greater stream acidification; however, Rock Creek exhibited lower trout metrics. Rock Creek was found to be decreasing in pH in the temporal trend analysis (Section 5.2). Further investigation is warranted to clarify what possible air/land disturbances and associated biogeochemical processes may be influencing water chemistry changes over time in Rock Creek. Adult rainbow trout densities were significantly greater in Lost Bottom Creek compared with Rock Creek.

In the large watersheds with sympatric trout populations, Palmer Creek had significantly greater YOY and adult brook trout densities and biomass compared with Cosby Creek and Walker Camp Prong (Table 16). Jakes Creek had significantly greater rainbow trout and adult brook trout densities and biomass compared with Cosby Creek, Palmer Creek, and Walker Camp Prong. These differences were not likely due to water quality effects, but rather biological factors associated with population dynamics and stream habitat at the broader basin scale.

6.2.4 Macroinvertebrates Metrics

In general, the macroinvertebrate metrics were in prescribed ranges of good or excellent stream conditions within the eight-block design watersheds (Table 17). EPT richness for the six sites ranged from 28.38 to 32.27, which is scored as good condition, being between the criteria of 28-35 (NCDENR 2011). The NCBI ranged from 1.86 to 2.47, which indicates streams in excellent condition. Although considered healthy biologically, NCBI scores in Rock Creek and Cosby Creek were significantly greater than the other sites, and water quality trends showed a declining pH over time at these sites. Final bioclassification scores, which are combined scores using EPT richness and the NCBI, ranged from 4.06 to 4.45 indicating an excellent to good stream condition.

Table 16. Comparison of fish metrics among GRSM eight-block design watersheds. Between two watersheds, metrics with $p < 0.05$ were significantly different; and among three or more watersheds, values with dissimilar letters were significantly different from each other ($p < 0.05$). Trout density (Den) and biomass (Biom) are in fish/100 m² and kg/ha, respectively.

	Fish type	Watersheds name	N	YOY Den	ADT Den	YOY Biom	ADT Biom	YOY K	ADT K
<i>Small watersheds</i>									
Allopatric sites	BKT	Road Prong	18	2.33	5.64	0.48	17.72	1.04	0.95
		Rock Creek	20	2.59	4.14	0.48	9.92	1.05	1.00
		p		0.36	0.05	0.94	<0.01	0.91	0.01
Sympatric sites	BKT	Lost Bottom	285	7.64	12.42	2.04	25.61	0.97	0.95
		Rock Creek	46	2.19	3.12	0.68	8.53	1.04	1.00
		P		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	RBT	Lost Bottom	122	0.41	1.70	0.06	6.83	0.96	0.94
		Rock Creek	28	0.19	0.68	0.02	3.56	1.05	0.99
		P		0.48	0.01	0.58	0.10	0.13	<0.01
<i>Large watersheds</i>									
Allopatric sites	BKT	Cosby	40	4.63	6.34	1.06	16.67	1.06	1.01
		Walker Camp	8	3.87	7.46	0.88	17.25	1.07	0.96
		p		0.55	0.15	0.55	0.58	0.78	0.03
Sympatric sites	BKT	Cosby	63	1.75 ^B	2.56 ^B	0.55 ^B	7.02 ^B	1.04 ^A	0.99 ^A
		Palmer	318	7.27 ^A	11.65 ^A	1.94 ^A	24.33 ^A	0.97 ^B	0.95 ^B
		Walker Camp	14	3.19 ^B	4.21 ^B	0.75 ^B	11.85 ^B	1.09 ^A	1.00 ^A
	RBT	Cosby	46	1.04 ^B	2.07 ^B	0.17 ^A	8.51 ^B	1.05 ^A	0.98 ^A
		Jakes	23	2.50 ^A	6.93 ^A	0.26 ^A	24.68 ^A	1.08 ^A	1.00 ^A
		Palmer	154	0.97 ^B	2.51 ^B	0.16 ^A	9.44 ^B	0.95 ^B	0.93 ^B
		Walker Camp	13	0.65 ^B	1.15 ^B	0.11 ^A	4.04 ^B	1.07 ^{AB}	1.00 ^A

Among the six eight-block design watersheds with macroinvertebrate data (Table 15), few significant differences were observed among the numerous metrics (Table 17). Richness of all functional feeding groups, EPT richness and abundance, total taxa richness and abundance, and functional feeding group abundances for predators and shredders were not significantly different among these six watersheds. Percent abundances of collector functional feeding groups were significantly different in Lost Bottom Creek and Palmer Creek compared with streams in the other four watersheds.

Table 17. Comparison of macroinvertebrate metrics among GRSM eight-block design watersheds. Tukey HSD method was used where significant differences ($p < 0.05$) are indicated by different letters on the same row.

Metrics		Small Watersheds			Large Watersheds		
		Lost Bottom	Road Prong	Rock Creek	Palmer	Walker Camp	Cosby
N		15	11	16	38	13	17
NCBI		1.86 ^B	2.11 ^{AB}	2.47 ^A	1.95 ^B	2.20 ^{AB}	2.44 ^A
EPT richness		30.73	32.27	28.38	32.08	29.54	28.76
EPT abundance		0.74	0.78	0.77	0.75	0.77	0.77
Final Bioclassification		4.21 ^{AB}	4.45 ^A	4.06 ^B	4.32	4.33	4.12
TR (Taxa richness)		49.00	49.73	48.06	52.13	45.92	48.59
Taxa abundance		325.33	341.73	316.69	358.92	323.54	321.06
Richness of functional feeding group	Collector-Filterer	7.07	5.82	5.88	7.21 ^A	5.08 ^B	6.12 ^{AB}
	Collector-Gatherer	10.60	10.45	11.56	12.08	9.54	11.76
	Predator	15.07	16.82	15.94	15.11	15.38	16.00
	Scraper	7.27	8.18	6.69	8.58	7.46	6.66
	Shredder	7.40	7.18	6.81	7.92	6.92	6.88
Abundance of functional feeding group	Collector-Filterer	20% ^A	13% ^B	10% ^B	21% ^A	8% ^B	14% ^B
	Collector-Gatherer	18% ^B	34% ^A	29% ^A	22% ^B	32% ^A	29% ^A
	Predator	28% ^B	21% ^B	25% ^{AB}	23%	21%	24%
	Scraper	15%	15%	11%	15% ^A	14% ^{AB}	11% ^B
	Shredder	19%	19%	21%	18%	22%	21%

7.0 Relationships among Watershed Characteristics, Water Quality, and Biotic Metrics

Effects of water quality on aquatic macroinvertebrates and fish communities were examined in this section through a series of statistical analyses. Analyses were conducted for spatially-collocated stream survey site sets only (Section 2.2.4), and variables used were from the following groups: watershed characteristics (Section 2.5, Table 3), stream water chemistry (Section 2.2.1), fish metrics (Section 2.2.2), and macroinvertebrate metrics (Section 2.2.3). They included:

- Effects of watershed characteristics on water quality
- Effects of water quality on biotic metrics
- Relationships among watershed characteristics, water quality, and trout metrics
- Effects of stream acidity on biotic metrics: 303(d) listed streams
- Biotic interactions

The main goal of these analyses was to identify possible links between water quality degradation from acidic deposition and biological condition in GRSM streams. In addition, analyses can provide some insight on valuable water quality parameters and biotic metrics that could be used as indicators in a long-term monitoring program.

7.1 Effects of Watershed Characteristics on Water Quality

7.1.1 Methods: Relationships among Watershed Characteristics on Water Quality

In this analysis, collocated sites from the water quality and biological stream surveys were used (Section 2.2.4), differing from the Section 6.2 analysis where eight-block design watersheds were used only. The number of stream survey sites for chemical parameters varied from 59 to 64. Two statistical analyses were utilized in this section; stepwise multiple regression and structural equation modeling.

Stepwise multiple regression models were developed for the following chemical parameters as dependent variables: pH, ANC, conductivity, chlorine, nitrate, sulfate, sodium, potassium, magnesium, calcium, and BCS. Median values for each chemical parameter and site were used. For model development, watershed characteristics were independent variables, and constituted a single unit value per site. Regression models were used to identify key watershed characteristics influencing different chemical parameters. Regression modeling was completed with JMP v.9.

A second statistical approach using structural equation modeling (SEM) was applied to these data (Arbuckle 2010). The goal of this modeling was to identify the dominant variables and significant linkages (pathways) between these variables. SEM is a multivariate technique representing, estimating, and testing a network of relationships between variables (measured variables and latent constructs). A *measured variable* is a variable that is directly measured whereas a *latent variable* is a construct, or an ordination factor that is not directly measured. A *latent variable* could be defined as whatever its multiple indicators have in common with each other. A third type of variable, termed an unobserved or unexplained variable, is only used in

model development and denoted by “e” numbers. SEM explains patterns of correlation/covariance among a set of all variable types, and as much variance as possible is specified with the model. SEM resolves problems of multicollinearity. Multiple measures are required to describe a latent construct (unobserved variable), and multicollinearity cannot occur because unobserved variables represent distinct latent constructs. A structural equation model is simply a statistical statement about the relationships among variables, where model output is represented by a graphical path diagram with numerical estimates of correlation and covariance coefficients. For a model, the null hypothesis is that the model is significant with $p > 0.05$, indicating that a constructed model can be successfully used to predict relationships in the path diagram. SEM was completed with use of SPSS AMOS software.

7.1.2 Results: Stepwise Multiple Regression Models

Stream acidity and acid anions were primarily controlled by average basin slope (slope) and the percent drainage area of underlying Anakeesta rock, and secondarily by different forest covers (Table 18). Increased pH was a function of decreased Anakeesta. Increased ANC was related to decreased elevation and slope; and increased BCS was related to lower slopes and Anakeesta. Although the Neff et al. (2013) study was specifically designed to address the question of whether Anakeesta plays a role in stream acidification, results were not as prominent as observed in this study's regression equation. Reasons for the differences may be Neff et al. (2013) used more recent water quality data, and a smaller number of stream sites. It also could be due to statistical collinearity because Anakeesta occurs along higher elevation ridges where slopes are naturally steeper. In general, results from the regression models for pH, ANC, and BCS reflect a trend of increased acidification in the steep-sloped watersheds typically found in the higher elevation areas of GRSM.

Although influenced by slope and Anakeesta, each acid anion differed slightly by its relationship with the watershed variable (Table 18). Both sulfate and chloride increased with increased Anakeesta, but sulfate increased with slope, whereas chlorine decreased. The observed differences between these two ions are likely due to differing deposition patterns and watershed ion transport processes. Sulfate deposition is greater in the higher elevation areas with steeper slopes and is controlled by soil absorption. Chlorine deposition is generally less than sulfate and nitrate, and it is relatively mobile through soil and groundwater; therefore, it appears that chlorine increases with drainage area (a surrogate variable for slope). Anakeesta is a potential source of stream sulfate, and the sulfate model selected Anakeesta by stepwise regression. The stepwise regression procedure finds the “best” model to fit the data, thus drainage area as a dominant independent variable may equally produce a statistically significant model. In this study, model development was restricted to the JMP program stepwise outputs. Interestingly, stepwise regression for nitrate did not select Anakeesta as an independent variable. Nitrate increased with increased slope, and this relationship is consistent with previous findings where nitrate concentrations were greater in headwater streams.

Regression models for base cations also selected slope and percent Anakeesta as primary watershed variables (Table 18). However, increased BCS and calcium were largely controlled by increasing drainage area and decreasing Anakeesta. The model for magnesium selected elevation rather than drainage area, but these two watershed variables are related. Increasing model slope was related to decreasing BCS and potassium, and increasing calcium. Soil acidification can cause calcium export (Mitchell et al. 1992), and increased concentrations in watersheds with

greater slopes could infer this export process. This result should be noted, because in the northern Appalachian region, calcium depletion from soils is a concern (Lawrence et al. 2009, Navrátil et al. 2010).

Table 18. Multiple regression models using watershed parameters as predictors for median stream chemical concentration. The unit for chemical concentrations was in $\mu\text{eq L}^{-1}$, except pH in pH unit. Units for watershed parameters are the same as presented in Table 3.

pH = 6.5948 – 0.7526 Anakeesta – 0.4686 Humic-Typic_Dystrudepts	N = 64, $R^2_{\text{Adj}} = 0.5843$, $p < 0.01$
ANC = 265.5408 – 0.1141Elevation -2.7376Slope	N = 64, $R^2_{\text{Adj}} = 0.5677$, $p < 0.01$
Cond = 17.5085 -24.5471Mesic_Oak – 7.2095Northern_Hardwood + 83.6887 Pine_Oak	N = 64, $R^2_{\text{Adj}} = 0.5368$, $p < 0.01$
Cl ⁻ = 117.8478 – 0.1848Slope + 2.2169Anakeesta + 7.5851Pine + 19.8967Tulip_Poplar	N = 64, $R^2_{\text{Adj}} = 0.3049$, $p < 0.01$
NO ₃ ⁻ = -7.0745 + 0.6185Slope – 47.9385Mesic_Oak + 12.9005V_Diff + 14.9635Humic-Typic_Dystrudepts	N = 64, $R^2_{\text{Adj}} = 0.6415$, $p < 0.01$
SO ₄ ²⁻ = 17.4667 + 1.6980 Slope + 13.1367 Anakeesta – 60.1677 Mesic_Oak + 47.7397 Xeric_Oak – 32.7224 V_Diff	N = 62, $R^2_{\text{Adj}} = 0.7108$, $p < 0.01$
Na ⁺ = 38.1825 + 80.2394 Pine – 50.1946 Spruce_Fir – 28.8345 Xeric_Oak	N = 64, $R^2_{\text{Adj}} = 0.6029$, $p < 0.01$
K ⁺ = 15.6060 – 0.2194 Slope – 3.6789 Anakeesta + 9.6593 Mixed_Mesic_Hardwood + 10.7665 Xeric_Oak	N = 64, $R^2_{\text{Adj}} = 0.7655$, $p < 0.01$
Mg ²⁺ = 72.9377620 – 0.0209 Elevation + 8.6537 Anakeesta + 14.8662 Cove_Hardwood – 35.8949 VDif	N = 60, $R^2_{\text{Adj}} = 0.6345$, $p < 0.01$
Ca ²⁺ = 45.9075 +0.0877 Area + 1.3834 Slope – 17.1878 Anakeesta – 34.2713 V_Diff	N = 59, $R^2_{\text{Adj}} = 0.4169$, $p < 0.01$
BCS = 160.9773 + 0.1547 Area – 1.5676Slope – 24.4695 Anakeesta – 56.2684S_Diff – 31.8984 Humic-Typic Dystrudepts	N = 61, $R^2_{\text{Adj}} = 0.6421$, $p < 0.01$

The regression models all contained significant, but to a lesser extent, watershed variables of various forest cover types (Table 18). The independent watershed variables in the regression model for sodium consist only of forest cover types, dominated by higher elevation pine and spruce. Sodium cycling in conifer forests and soil export regulation to streams has been described by Draaijers et al. (1997), Ferm and Hultberg (1999), Oyarzún et al. (2004), and others. The importance of this biogeochemical process in GRSM is not known, although some

indication of potassium and sodium forest cycling was reported by Cai et al. (2010) in the Noland Divide watershed.

7.1.3 Results: structural equation modeling

A structural equation model (SEM) was developed for watershed characteristics and stream chemistry (water quality) parameters, relating the variables and graphically representing them in a path diagram containing estimates of correlation and covariance coefficients (Section 7.1.1). Two latent variables, watershed and water_quality, are shown in elliptical blocks (Fig. 23) and represent ordination factors (eigenvectors explaining the most data variance). These two latent variables were correlated ($r = 0.89$) and approximately 79% of the variance was explained by the overall SEM ($\chi^2 = 17.596$, $p = 0.550$, $df = 19$). Four measured watershed variables fit best in the SEM; they were mean elevation ($r = 0.82$), soil hydraulic conductivity ($r = 0.78$), area of spruce-fir forest cover ($r = 0.68$), and basin area ($r = -0.24$). Most of the variance was explained by mean elevation (67%), and soil hydraulic conductivity (61%). The four water quality parameters that fit best in the SEM were pH ($r = -0.89$), nitrate ($r = 0.78$), sodium ($r = -0.77$), and potassium ($r = -0.83$). Most of the variance was explained for the water_quality latent variable by pH at 80%. The other three chemical variables ranged between 59% and 68%. SEM model output is consistent with other findings, inferring that water quality survey sites in smaller basins at higher elevations dominated by spruce-fir forest, having greater soil hydraulic conductivity (faster interflow rates) will have lower stream pH, lower sodium and potassium concentrations, and higher nitrate concentrations. The SEM did not select for the water_quality latent variables of sulfate, calcium, or magnesium. This finding may reflect geochemical process regulation controlling ion export from soils to streams.

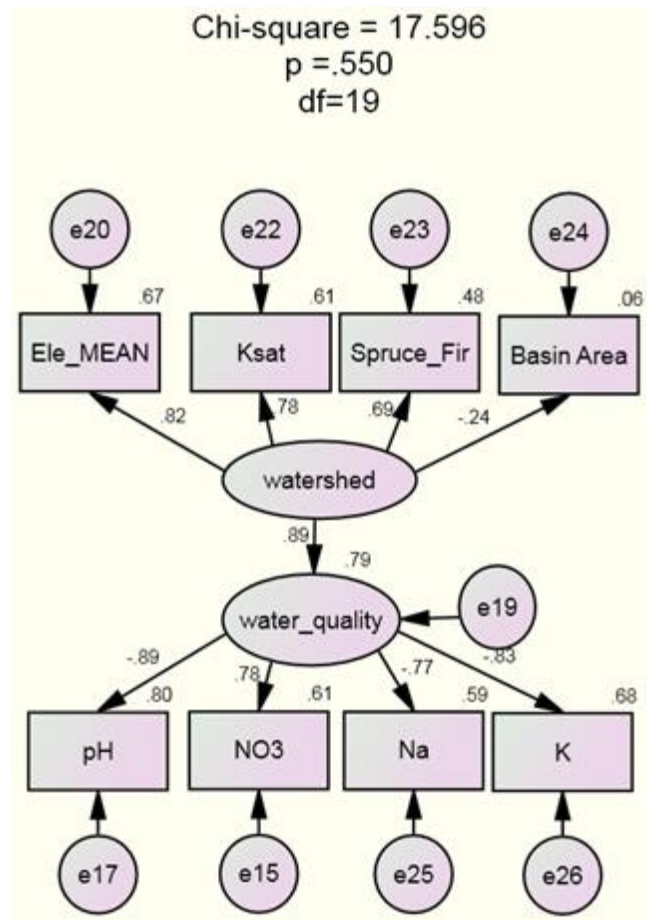


Figure 23. Structural equation model between watershed characteristics and stream chemistry using median chemical concentrations for collocated GRSM water quality and biological survey sites (1993-2009). Mean elevation (Ele_MEAN), soil hydraulic conductivity (Ksat), Spruce_Fir, and Basin Area are defined in Table 3.

7.2 Effects of Water Quality on Biotic Metrics

7.2.1 Methods: Effects of Water Quality on Biotic Metrics

A non-parametric Kendall's tau correlation analysis was conducted between chemical parameters and trout and macroinvertebrate metrics (Section 7.2.2). Chemical parameters of pH, ANC, conductivity, chlorine, nitrate, sulfate, sodium, potassium, magnesium, calcium, and BCS, as well as ammonia and dissolved metals (Al, Cu, Fe, Mn, Si, and Zn) were dependent variables. Kendall's tau correlation analysis was completed with JMP v.9 software.

Two additional approaches that were used to identify statistical relationships among stream chemistry parameters and trout and macroinvertebrate metrics were: 1) logistic stepwise regression modeling using JMP v.9, and 2) SEM using SPSS AMOS software (Sections 7.2.3 and 7.3.4). Results of these analyses provide predictive significance, while the non-parametric analysis using the Kendall's tau correlation analysis does not. Chemical parameters as dependent variables were limited to: pH, ANC, conductivity, Cl^- , NO_3^- , SO_4^{2-} , NH_4^+ , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and BCS because dissolved metals analysis began in 2003 and macroinvertebrate surveys ended that year along with a majority of trout surveys. The equation for predicting dissolved aluminum

concentrations could not be used in the regression models because of collinearity with proton (pH) and sulfate concentrations (Section 2.4.1).

Stream chemistry data were compiled differently in this statistical analysis in order to better match chemical exposure periods for adult and YOY with fish survey date (Table 19). For YOY trout, one-year average chemistries corresponding to the fish collection dates were used as the potential independent variables in the regression models. For adult trout, three-year average chemistries corresponding to the fish collection dates were used. Brook trout spawn in late summer and early fall, and fry emerge in the fall. Rainbow trout spawn and fry emerge in the spring. This analysis specifically attempts to examine effects of water quality on trout recruitment. Water chemistries in the designated periods were averaged and used as independent variables for the stepwise regression modeling effort.

Similarly, stream chemistry data were compiled by macroinvertebrate survey year, averaging each parameter for that collection year. The approach also attempts to match chemical exposures with the year biological data were collected. Water chemistries were used as independent variables for the stepwise regression modeling effort.

Table 19. Data compilation for averaging water chemistries associated with trout exposure periods.

Trout species	Age group	Water chemistry: period data averaged
Brook trout	YOY	September of prior year to fish sampling date
	Adult	September of three years prior to fish sampling date
Rainbow trout	YOY	March of prior year to fish sampling date
	Adult	March of three years prior to fish sampling date

7.2.2 Results: Kendall's Tau Correlation Analysis

Correlation coefficients among chemical parameters and biotic metrics were generated by the Kendall's tau correlation analysis, comprehensively including trout and macroinvertebrate metrics (Table 20). Chemical parameters included pH, ANC, BCS, conductivity, acid anions, base cations, and dissolved metals. Measured and computed aluminum were both used in the analysis (Section 2.4.1). The complete set of correlation coefficients and significant levels are in Appendix 12.

Stream acidity, as measured by pH and ANC, was significantly correlated inversely with adult brook trout (density and biomass) and directly with YOY and adult rainbow trout (density and biomass) for all data including sympatric and allopatric populations (Table 20). BCS followed the same correlation patterns as with pH and ANC. BCS served as a better chemical variable to interpret than base cations individually (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) because of inconsistent correlations among the base cations. Stream nitrate directly correlated with density and biomass for YOY and adult brook trout, while nitrate inversely correlated with YOY and adult rainbow trout. Sulfate concentrations were inversely correlated with YOY brook and rainbow trout, and adult rainbow trout. Likewise, elevated concentrations of dissolved aluminum correlated with reduced densities and biomass of YOY brook and rainbow trout, and adult brook trout. These correlations indicate that streams with lower pH, ANC, and BCS, and higher nitrate concentrations had higher densities and biomass of brook trout; and inversely streams with higher pH, ANC, and BCS, and lower nitrate concentrations had higher densities and biomass of rainbow trout. With this analysis utilizing both allopatric and sympatric data, outcomes were likely due to: 1) brook trout were generally located in the higher elevation streams and rainbow trout in the lower elevation streams where distributions may be influenced by interspecific competition (Fig. 17), and 2) lower pH, ANC, and BCS, and higher nitrate concentrations were measured in the higher elevation streams compared with lower elevation streams (Section 6.1.2). Because stream sulfate concentrations did not differ along a longitudinal gradient in GRSM, correlations with trout metrics could not be attributed to this watershed factor. These results infer that sulfate concentration may be the best water quality indicator of biological effects due to stream acidification from a park-wide perspective.

In order to separate the potential effects of interspecific competition, and indirectly, stream chemistry changes along elevation gradients, sites only with allopatric populations were used in a Kendall's tau correlation analysis (Table 21). For allopatric brook trout populations, both adult and YOY density and biomass were directly correlated with pH, ANC, and BCS, and inversely correlated with sulfate and aluminum concentrations. YOY brook trout biomass was inversely correlated with nitrate concentrations. From these results, it appears that brook trout adults and YOY were similarly affected by stream acidification. In GRSM, Neff et al. (2009) found chronic stress responses with stormflow episodic acidification and dissolved aluminum concentrations in adult brook trout, and suggested that YOY may be more susceptible than adults.

Allopatric rainbow trout populations, typically found in the lower watershed areas, were not as correlated with chemical parameters as with the brook trout (Table 21). Allopatric rainbow trout populations, both adult and YOY, density and biomass were directly correlated with ANC and BCS. YOY rainbow trout were inversely correlated with sulfate, nitrate, and aluminum concentrations, but adult were not. This suggests that YOY may be more vulnerable than adults to the toxicological effects of dissolved aluminum (Section 4.1, Appendix 10).

Table 20. Correlation coefficients among stream chemistry and biotic indexes for all collocated sites (1993-2009) using the Kendall's tau correlation analysis. Al = measured dissolved aluminum from 2003-2009, and Al* = computed dissolved aluminum based on $[H^+]$ and $[SO_4^{2-}]$ as defined in Section 2.4.1. Only the coefficients with significance level $p < 0.05$ are presented.

		pH	ANC	Cond	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BCS	Al*	Al	Cu	Fe	Mn	Si	Zn
YOY BKT	Density			-0.11		0.15	-0.15			0.11					-0.31					
	Biomass			-0.14		0.11	-0.19			0.12		-0.10			-0.32					
	K		-0.11	0.17	-0.12	0.15	0.16				0.12		-0.11	0.15						
ADT BKT	Density	-0.15	-0.20		0.17	0.30		-0.16	0.12				-0.24		-0.23		0.21		-0.23	
	Biomass	-0.16	-0.20		0.15	0.35		-0.21	0.16	-0.12			-0.21				0.22		-0.30	
	K			0.16		0.20	0.12				0.15		-0.11						-0.27	
YOY RBT	Density	0.15	0.27			-0.14	-0.15	0.24		0.25	0.15	0.13	0.27	-0.27	-0.46			-0.46		-0.36
	Biomass	0.23	0.35	0.17		-0.15	-0.14	0.32		0.30	0.21	0.17	0.34	-0.33	-0.33			-0.50	0.41	
	K		0.12		-0.13		-0.13													
ADT RBT	Density	0.15	0.16			-0.20	-0.20			0.20			0.16							
	Biomass	0.25	0.26			-0.21	-0.13			0.27		0.14	0.25		0.42					
	K					0.18			-0.13											
NCBI				0.24			0.18				0.22	0.20								
EPT richness		0.21	0.24	-0.16		-0.15	-0.16	0.13		0.26			0.21	-0.22						
EPT abundance			-0.15			0.13		-0.14					-0.13							
Final Bioclassification			0.16							0.19			0.17	-0.16						
Taxa Richness		0.23	0.32	-0.17		-0.17	-0.23	0.22		0.27			0.27	-0.26						
Taxa Abundance		0.22	0.27	-0.11			-0.19	0.17		0.25			0.32	-0.28						
Richness of Functional Feeding Group	Filterer	0.24	0.26			-0.21		0.15		0.17			0.29	-0.29						
	Gatherer	0.19	0.33	-0.14		-0.16	-0.28	0.31	0.15	0.34			0.28	-0.28						
	Predator		0.15				-0.12			0.15										
	Scraper	0.33	0.36	-0.19		-0.21	-0.24	0.20		0.23			0.35	-0.35						
	Shredder	0.25	0.25	-0.16			-0.22	0.19		0.22			0.20	-0.21						
Abundance of Functional Feeding Group	Filterer			-0.14		-0.18														
	Gatherer					0.12														
	Predator										-0.12	-0.16								
	Scraper	0.23	0.19			-0.12							0.21	-0.22						
	Shredder		-0.12					-0.14		-0.18			-0.11							

Table 21. Correlation coefficients among stream chemistry and fish metrics for collocated sites (1993-2009) with only allopatric populations, using the Kendall's tau correlation analysis. Al = measured dissolved aluminum from 2003-2009, and Al* = computed dissolved aluminum based on $[H^+]$ and $[SO_4^{2-}]$ as defined in Section 2.4.1. Only the coefficients with significance level $p < 0.05$ are presented.

		pH	ANC	Cond	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BCS	Al*	Al
YOY BKT	Density	0.23	0.38	-0.26			-0.41	0.38		0.23		-0.16	0.27	-0.28	
	Biomass	0.28	0.42	-0.28		-0.16	-0.44	0.42		0.20		-0.20	0.32	-0.35	
	K			0.15	-0.17	0.18	0.17				0.19				
ADT BKT	Density	0.40	0.41	-0.18	0.17		-0.44	0.39		0.38			0.33	-0.36	-0.42
	Biomass	0.45	0.46				-0.42	0.41		0.27			0.43	-0.45	-0.45
	K			0.28		0.32	0.21			-0.25	0.38	0.21			
YOY RBT	Density		0.39			-0.45							0.38	-0.37	
	Biomass	0.44	0.54			-0.57	-0.42	0.42					0.50	-0.50	
	K	0.41									0.47	0.58	0.63	-0.43	
ADT RBT	Density		0.45										0.45		
	Biomass		0.43										0.43		
	K														

Several macroinvertebrate metrics were directly correlated with stream pH, ANC, BCS, and sodium and potassium concentrations (Table 20). They were: taxa richness and abundance, EPT richness, and richness of the filterer, gatherer, scraper, and shredder functional feeding groups. With this same group of metrics, sulfate concentrations were inversely correlated. Computed dissolved aluminum concentrations were also inversely correlated with these macroinvertebrate metrics, which was logical considering the predictive model for aluminum is a function of sulfate and proton concentrations (pH). The NCBI was directly correlated with sulfate concentrations, indicating that more intolerant species were found in streams with higher sulfate.

7.2.3 Results: Effects of Water Quality on Trout

Relationships between stream chemical parameters and trout metrics were statistically analyzed by stepwise multiple regression modeling and structural equation modeling.

Stepwise Multiple Regression. Adult and YOY brook trout density and biomass were best predicted directly with nitrate and inversely with sulfate (Table 22). Additionally, YOY brook trout density and biomass regression models were inversely related to pH and directly related to potassium concentrations, and adult brook trout biomass with calcium. The regression model resulted in an outcome similar to the Kendall's tau correlation analysis, where increased brook trout metrics were significantly related to lower pH and higher nitrate concentrations. These statistical outcomes appear to be due to longitudinal gradients of chemistry and brook trout metrics from low to high elevation streams. Regression modeling differed from the Kendall's tau analysis with the base cations, where potassium and calcium were directly related to brook trout metrics rather than the inversely related composite estimate per BCS. The model selection of potassium is likely due to watershed factors which the collocated sites represent, and not due to any indirect biogeochemical effect on brook trout populations.

Brook trout metrics were inversely related to increased sulfate concentrations, inferring this relation may represent an acidification response. However, sulfate was not selected in the logistic stepwise procedure for the predictive equation generated for rainbow trout (Table 22). Adult rainbow trout density and biomass were inversely related to nitrate concentration; this result likely reflects the rainbow trout distribution range and lower nitrate concentrations observed in the lower elevation stream sites. The observation that adult rainbow trout were also directly related with ammonia is difficult to explain, except that this result may be influenced by the low ammonia concentrations and is an artifact of statistical scaling. Although significant ($p < 0.01$), the regression models for rainbow trout generally had small correlation coefficients ($R^2_{Adj} < 0.25$) compared with brook trout ($0.04 < R^2_{Adj} < 0.57$). Regression models for condition factor K had smaller correlation coefficients ($R^2_{Adj} < 0.15$) than for density and biomass metrics.

Structural Equation Modeling. SEM provides a statistical approach to examine outcomes from best-fit model development that incorporates all variables, rather than restricting model development to a single dependent variable. Models with water quality were developed using biomass and condition factor K metrics for brook and rainbow trout (Fig. 24). Density was not used due to collinearity with biomass. In these SEMs, the latent variable in elliptical boxes included water_quality, and brook trout (BKT) or rainbow trout (RBT). Latent variables were not measured quantities, but rather represented ordination factors. Between these latent variables for water_quality and BKT, the model was highly correlated ($r = -0.94$) with 88% of the variance explained ($\chi^2 = 18.092$, $p = 0.383$, $df = 17$). The negative sign for the correlation coefficient is

Table 22. Multiple regression models to predict trout metrics using stream chemistry concentrations ($\mu\text{eq L}^{-1}$, pH units, and conductivity in $\mu\text{S/cm}$) for GRSM collocated water quality and fish survey sites, 1993 to 2009.

Brook Trout

YOY_Den = $30.0186 - 4.1366 \text{ pH} + 0.3539 [\text{NO}_3^-] - 0.3566 [\text{SO}_4^{2-}] + 0.3601 [\text{K}^+]$	N = 195, $R^2_{\text{Adj}} = 0.440$, $p < 0.01$
YOY_Biom = $9.5809 - 1.3164 \text{ pH} + 0.1128 [\text{NO}_3^-] - 0.1207 [\text{SO}_4^{2-}] + 0.1248 [\text{K}^+]$	N = 195, $R^2_{\text{Adj}} = 0.407$, $p < 0.01$
YOY_K = $0.9165 + 0.0027 [\text{SO}_4^{2-}]$	N = 174, $R^2_{\text{Adj}} = 0.075$, $p < 0.01$
ADT_Den = $9.2839 + 0.7448 [\text{NO}_3^-] - 0.5775 [\text{SO}_4^{2-}]$	N = 163, $R^2_{\text{Adj}} = 0.570$, $p < 0.01$
ADT_Biom = $12.2683 + 1.5719 [\text{NO}_3^-] - 1.2577 [\text{SO}_4^{2-}] + 0.1872 [\text{Ca}^{2+}]$	N = 163, $R^2_{\text{Adj}} = 0.536$, $p < 0.01$
ADT_K = $0.8786 + 0.0100 \text{ Cond} + 0.0015 [\text{NO}_3^-] - 0.0015 [\text{Ca}^{2+}]$	N = 159, $R^2_{\text{Adj}} = 0.155$, $p < 0.01$

Rainbow Trout

YOY_Den = $-1.0150 + 0.3385 [\text{K}^+]$	N = 163, $R^2_{\text{Adj}} = 0.105$, $p < 0.01$
YOY_Biom = $-1.4172 + 0.2128 [\text{K}^+] + 0.0129 \text{ BCS}$	N = 162, $R^2_{\text{Adj}} = 0.202$, $p < 0.01$
YOY_K = $0.9770 + 0.0001 \text{ BCS}$	N = 141, $R^2_{\text{Adj}} = 0.040$, $p = 0.01$
ADT_Den = $4.0489 - 0.1076 [\text{NO}_3^-] + 0.5615 [\text{NH}_4^+]$	N = 133, $R^2_{\text{Adj}} = 0.118$, $p < 0.01$
ADT_Biom = $4.6611 - 0.4030 [\text{NO}_3^-] + 3.6483 [\text{NH}_4^+] + 1.2142 [\text{K}^+]$	N = 133, $R^2_{\text{Adj}} = 0.255$, $p < 0.01$
ADT_K = $0.9379 + 0.0028 [\text{NO}_3^-] - 0.0132 [\text{NH}_4^+]$	N = 133, $R^2_{\text{Adj}} = 0.132$, $p < 0.01$

only relative to the measured variables. As the SEM null hypothesis, a model is considered significant, or correct when $p > 0.05$. The model for water_quality and RBT was less correlated ($r = 0.57$) than for the BKT model, and only 33% of the variance was explained ($\chi^2 = 35.212$, $p = 0.050$, $\text{df} = 23$).

The water_quality-BKT SEM was best explained by increased YOY condition factor K with decreased pH, ANC, sodium and potassium, and increased nitrate (Fig. 24). Correlation coefficients (r) for pH, ANC, and nitrate were 0.94, 0.92, and -0.75 with 89%, 94%, and 57% of the variance explained, respectively. It appears this model result reflects the collocation of brook trout in higher elevation streams and the water chemistry in these headwater streams. This result, particularly with nitrate, was also observed with Kendall's tau correlation and multiple regression analyses. Increased YOY condition factor K was found to relate to increased sulfate ($r = -0.45$) with 20% of the variance explained. This result is opposite of what one would expect but the variance explained was low. Sulfate showed significant covariance with ANC (shown on the SEM by the arching double arrowed line, with a COV of 0.53). Likewise, as would be expected, pH and ANC co-varied. The SEM suggests that sulfate may have a significant control on ANC and pH from a park-wide perspective, where specific watershed characteristics related to sulfate export may dominate over longitudinal gradient patterns of nitrate concentrations.

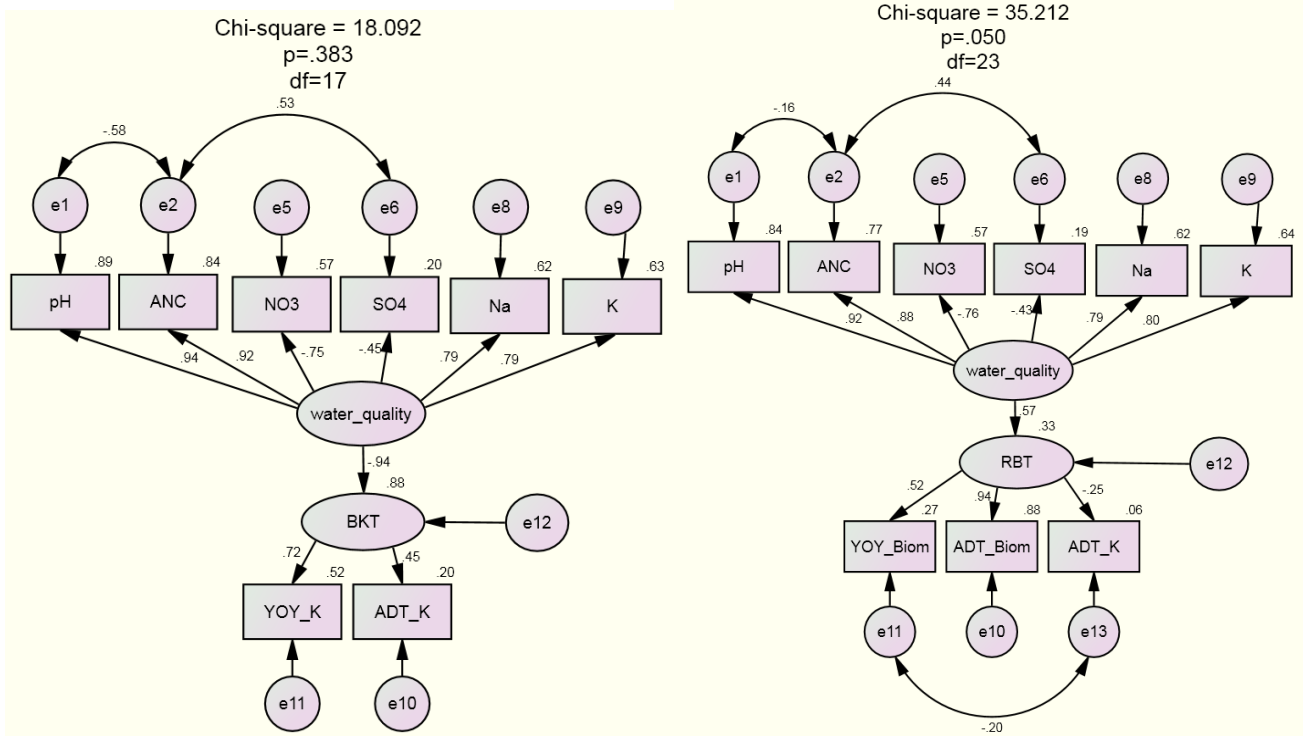


Figure 24. Structural equation models for water quality (median chemical parameters) and brook and rainbow trout metrics in GRSM collocated stream survey sites.

With the *water_quality*-*BKT* SEM, the correlation coefficient (r) for YOY condition factor K was 0.72, and 52% of the variance was explained (Fig. 24). The SEM also selected adult condition factor K, but it only added 20% of the variance explained. The failure of the model to select YOY and adult biomass as a *BKT* measured variable was a concern because regression models found biomass more correlated with chemical parameters than the condition factor K. However, the observation that water quality with trout metrics patterns were similar to outcomes of other statistical approaches provides stronger evidence to confirm the computed relationships.

The *water_quality*-*RBT* SEM was best explained by increased YOY and adult biomass and decreased condition factor K with increased pH, ANC, sodium and potassium, and decreased nitrate and sulfate (Fig. 24). Correlation coefficients (r) for pH, ANC, nitrate and sulfate were 0.92, 0.88, -0.67, and -0.43 with 84%, 77%, 57%, and 19% of the variance explained, respectively. This SEM was also similar to other statistical analyses relating rainbow trout biomass to stream chemistry found in lower elevation streams, except for sulfate. Streams with higher concentrations of sulfate appeared to be lower in YOY and adult trout biomass; however only 19% of the variance was explained by this chemical parameter. Similarly with the *BKT* SEM model, sulfate and ANC, and ANC and pH co-varied ($COV = 0.44$ and -0.16 , respectively).

7.2.4 Results: Effects of Water Quality on Macroinvertebrates

Relationships between chemical parameters and macroinvertebrate metrics were statistically analyzed by stepwise multiple regression modeling and structural equation modeling approaches.

Stepwise Multiple Regression. With 15 macroinvertebrate metrics as dependent variables, significant regression models were developed through logistic stepwise procedures ($p < 0.01$).

Although significant, model variables were not highly correlated ($0.047 < R^2_{\text{Adj}} < 0.283$). Results appear to be influenced by elevation trends for both macroinvertebrate and water chemistries, as described in Section 6.1.3 (Table 12). Macroinvertebrate metrics were influenced by pH and nitrate, and strongly by ANC (Table 23). For example, the North Carolina Biotic Index (NCBI), taxa richness (TR), scraper and shredder richness (RSCR, RSHR), and scraper abundance (ASCR) increased with increased pH or ANC. Stream pH and ANC were lower in the higher elevation streams and the macroinvertebrate metrics also were lower. As described by the River Continuum Concept (Vannote et al. 1980), scrapers would naturally be positioned in lower elevation stream reaches, while shredders would prefer higher elevation reaches. RSHR displayed no significant relationship with elevation (Table 12). Results could infer that shredders were affected by stream acidification in GRSM high elevation headwater areas, but further investigation is warranted.

Regression model relationships for richness and abundance of collector-filters (RCFI, ACFI) with nitrate follow elevation trends (Tables 12, 23). An inverse relationship reflects the natural watershed positioning of collector-filters down gradient of headwater areas, and with lower nitrate concentrations found in streams at those elevations. Abundance of collector-gatherers (ACGA) was directly related with stream nitrate.

Table 23. Multiple regression models to predict macroinvertebrate metrics using stream chemistry concentrations ($\mu\text{eq L}^{-1}$, pH units, and conductivity $\mu\text{S/cm}$) for GRSM collocated water quality and macroinvertebrate sites. Al* = estimated dissolved aluminum (Section 2.4.1). Macroinvertebrate metric abbreviations are on page xxi.

NCBI = $1.4048 + 0.0102 \text{ ANC} + 0.0146 [\text{SO}_4^{2-}]$	N = 140, $R^2_{\text{Adj}} = 0.2500$, $p < 0.01$
EPTR = $31.3294 + 0.3217 [\text{Cl}^-] - 0.1727 [\text{Mg}^{2+}] - 41.2962 [\text{Al}^*]$	N = 141, $R^2_{\text{Adj}} = 0.2835$, $p < 0.01$
EPTA = $0.8348 - 0.0027 [\text{Na}^+]$	N = 141, $R^2_{\text{Adj}} = 0.0470$, $p = 0.01$
TR = $39.7338 + 0.3302 \text{ ANC}$	N = 141, $R^2_{\text{Adj}} = 0.2094$, $p < 0.01$
TA = $137.129 + 25.132 [\text{K}^+]$	N = 89, $R^2_{\text{Adj}} = 0.1316$, $p < 0.01$
RCFI = $5.3625 + 0.1250 [\text{Cl}^-] - 0.1272 [\text{NO}_3^-] + 0.0479 [\text{Ca}^{2+}]$	N = 141, $R^2_{\text{Adj}} = 0.2368$, $p < 0.01$
RCGA = $6.1623 - 0.0575 [\text{SO}_4^{2-}] + 0.2554 [\text{Na}^+]$	N = 140, $R^2_{\text{Adj}} = 0.2399$, $p < 0.01$
RPRE = $16.7306 - 0.0668 [\text{SO}_4^{2-}]$	N = 140, $R^2_{\text{Adj}} = 0.0817$, $p < 0.01$
RSCR = $-7.4156 + 2.5213 \text{ pH} - 10.7125 [\text{Al}^*]$	N = 141, $R^2_{\text{Adj}} = 0.2561$, $p < 0.01$
RSHR = $-4.0730 + 1.8397 \text{ pH}$	N = 141, $R^2_{\text{Adj}} = 0.1103$, $p < 0.01$
ACFI = $-0.1805 - 0.0026 [\text{NO}_3^-] + 0.0009 [\text{Ca}^{2+}]$	N = 141, $R^2_{\text{Adj}} = 0.0907$, $p < 0.01$
ACGA = $0.2448 + 0.0029 [\text{NO}_3^-] - 0.0013 [\text{SO}_4^{2-}]$	N = 141, $R^2_{\text{Adj}} = 0.0772$, $p < 0.01$
APRE = $0.2529 - 0.0009 [\text{Ca}^{2+}]$	N = 141, $R^2_{\text{Adj}} = 0.0932$, $p < 0.01$
ASCR = $-0.4171 + 0.0831 \text{ pH} + 0.0010 [\text{SO}_4^{2-}]$	N = 140, $R^2_{\text{Adj}} = 0.1906$, $p < 0.01$
ASHR = $0.2767 - 0.0074 [\text{K}^+]$	N = 140, $R^2_{\text{Adj}} = 0.0531$, $p < 0.01$

As with the trout metric models, because elevation trends were not significant, higher sulfate concentrations could potentially infer acidification impairment (Table 12). The NCBI increased directly with sulfate, suggesting more tolerant species were related to higher sulfate concentrations (Table 23). Richness of predators (RPRE) and ACGA decreased as sulfate increased. Sulfate concentrations may indicate a toxicological relationship with more sensitive benthic macroinvertebrates, but it was not consistently selected by the logistic regression modeling. Estimated dissolved aluminum concentrations, a surrogate of sulfate and proton concentrations, were also found to be inversely related to EPT richness and RSCR.

Structural Equation Modeling. A significant SEM was generated, but latent variables water_quality and macroinvertebrates were weakly correlated ($r = 0.52$) and only 27% of the variance was explained ($\chi^2 = 35.852$, $p = 0.074$, $df = 25$) (Fig. 25). The three measured variables correlating with the latent variable macroinvertebrates included EPT richness, and taxa abundance and richness ($r = 0.86$, 0.75 , and 0.94), in which the variances explained were 74%, 56%, and 88% respectively. The chemical parameters selected by the SEM followed that reported for the trout metrics, including the covariance relationship between ANC and sulfate.

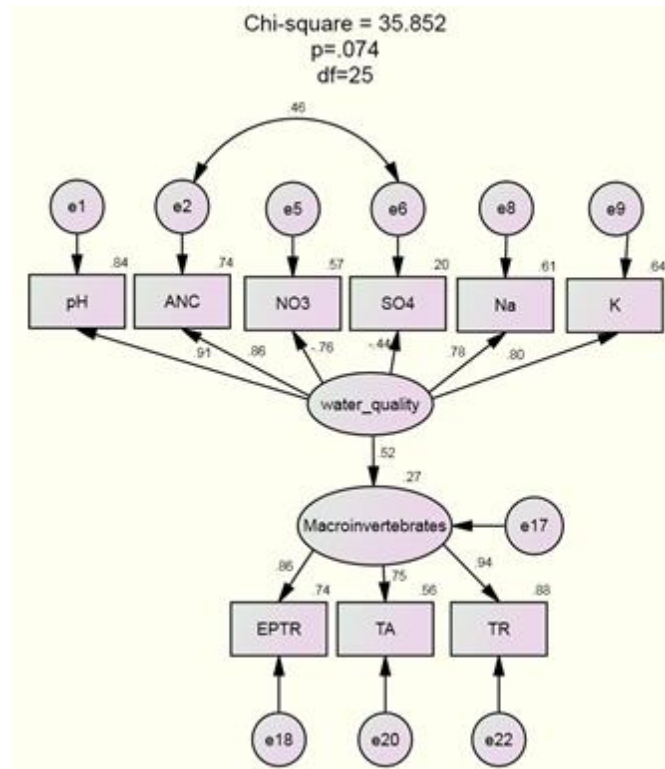


Figure 25. Structural equation models for water quality (median chemical parameters) and macroinvertebrate metrics in GRSM collocated stream survey sites.

7.3 Relationships among Watershed Characteristics, Water Quality, and Trout

An SEM was developed to examine multivariate relationships among watershed characteristics, water chemistry, and trout metrics. The goal of this statistical modeling effort was to identify the dominant variables and significant linkages or interrelationships (pathways) among the dominant variables collectively (Fig. 26).

Statistically significant SEMs were developed for brook and rainbow trout ($p = 0.144$, 0.288 , respectively). These SEMs consistently merged the outcomes of the individual models as reported for watershed - water_quality (Section 7.1.3), BKT - water_quality, and RBT - water_quality (Sections 7.2.3 and 7.2.4). Within the watershed-water_quality-BKT model, the latent variable watershed was correlated with the latent variable water_quality ($r = 0.89$) with 79% of the variance explained, and water_quality was correlated with the latent variable BKT ($r = 0.93$) with 79% of the variance explained. Within the watershed-water_quality-RBT model, the latent variable watershed was similarly correlated with the latent variable water_quality (as per the BKT model), but water_quality was correlated with the latent variable RBT ($r = -0.70$) with 49% of the variance explained.

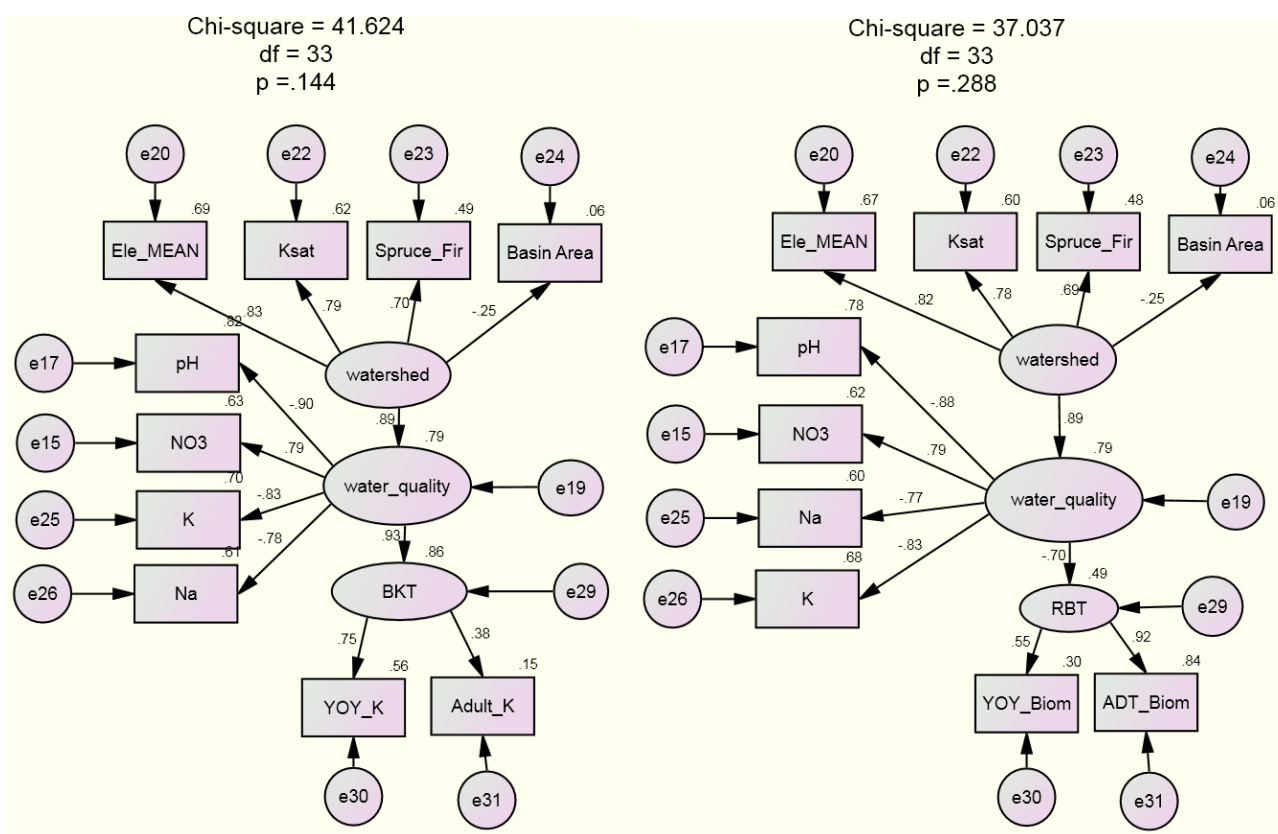


Figure 26. Structural equation models among watershed, water quality, and brook/rainbow trout metrics in GRSM collocated stream survey sites using the median chemical concentrations and trout metrics.

The SEMs (Fig. 26) illustrate the dominance of site elevation on stream chemistry (pH units; nitrate, potassium, and sodium concentrations) and trout metrics (condition factor K for brook trout and biomass for rainbow trout). Watershed characteristics with model significance also included soil hydraulic conductivity (Ksat), basin area, and percent cover of spruce-fir forest, which likewise are generally associated with elevation. Compared with the water quality_trout SEMs, the one difference with this SEM selection of chemical parameters was that ANC and sulfate were not included in the broader model with watershed characteristics. This difference was likely due to sulfate not being correlated with elevation (Table 12), and ANC co-varying with sulfate (Figs. 24, 25).

7.4 Effects of Acidity on Aquatic Biota in 303(d) Listed Streams

7.4.1 Methods: Effects of Stream Acidity on Biotic Metrics

Streams designated as acidity impaired by state Water Quality Standards, compiled as 303(d) listed streams, are those streams measured with a pH below 6.0. A stream pH below 6.0 is known to be potentially harmful to trout and other aquatic organisms (Chapter 4). In GRSM, 12 streams are 303(d) listed as impaired from acidification (Table 2), and their locations are shown in Figure 1.

In this analysis, a toxicologically significant pH was selected as 6.0 and used to group streams that were either above or below this pH criterion. Stream pH values for stormflow as determined by methods defined in Section 2.3, were summarized for collocated biological survey sites (Section 2.2.5). It should be noted that only five collocated water quality site sets had a median pH < 6.0, which were from stormflow samples (Table 2). In order to include more sites into this analysis, non-collocated trout and macroinvertebrate survey sites located in 303(d) listed streams were also added to the group with median pH < 6.0. Within each pH class (< or > pH 6.0), trout and macroinvertebrate metrics were summarized. Trout survey sites were separated into allopatric and sympatric population classes, assessing potential effects of fish competition. Generally, allopatric brook trout populations occur in higher elevation streams, and allopatric rainbow trout are in lower elevation streams (Fig. 17). Sympatric populations occur between elevation ranges of the two allopatric trout populations.

A student's t-test was used to test for significant differences among the biotic metrics between the two pH classified stream groups. Of the trout metrics, stream sites were also grouped into allopatric and sympatric brook and rainbow trout populations. The student's t test was completed using JMP v.9 software.

7.4.2 Results: Acidity Effects on Trout

Metrics for allopatric brook trout were significantly greater in streams with a pH > 6.0 than where pH < 6.0; metrics included YOY density and biomass, adult density and biomass, and YOY condition factor K ($p < 0.01$) (Table 24). Only adult condition factor K was not significant ($p = 0.09$). Because these allopatric populations are only found in higher elevation streams, no elevation trend should affect this statistical analysis. A pH of 6.0 was recognized as a toxicological threshold from the literature review (Table 8), and results in this study suggest it is a relevant threshold for GRSM brook trout streams.

Metrics for allopatric rainbow trout were significantly greater in streams with a pH > 6.0 than where pH < 6.0, but only for YOY density and biomass ($p = 0.02$, < 0.01 , respectively). Results

Table 24. Comparison of mean biotic metrics for brook and rainbow trout in collocated streams with median stormflow pH > 6.0 and < 6.0 in GRSM. p = significance level. Trout density (Den) and biomass (Biom) are in fish/100 m² and kg/ha, respectively.

			YOY Den	ADT Den	YOY Biom	ADT Biom	YOY K	Adult K
Allopatric sites								
BKT	Streams with pH > 6	Mean	10.17	16.86	2.97	37.04	1.00	0.97
		N	119	119	118	119	117	119
	Streams with pH < 6	Mean	3.51	6.40	0.74	15.47	1.07	0.99
		N	47	48	47	48	44	48
	p	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.09
RBT	Streams with pH > 6	Mean	6.16	3.65	4.98	22.78	1.03	0.96
		N	35	35	35	35	30	35
	Streams with pH < 6	Mean	1.51	2.87	0.43	11.45	1.00	1.00
		N	10	10	10	10	7	9
	p	0.02	0.54	<0.01	0.08	0.86	0.14	
Sympatric sites								
BKT	Streams with pH > 6	Mean	3.05	3.99	0.91	9.93	0.99	0.93
		N	96	98	96	98	80	95
	Streams with pH < 6	Mean	1.83	2.90	0.54	7.93	1.02	0.97
		N	75	76	75	76	65	75
	p	0.02	0.38	0.01	0.87	0.10	<0.01	
RBT	Streams with pH > 6	Mean	3.29	3.91	2.09	19.17	1.04	0.96
		N	188	192	187	192	171	191
	Streams with pH < 6	Mean	0.58	2.42	0.12	11.63	0.93	1.00
		N	47	50	47	50	27	49
	p	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

may reflect the low number of sample events (N = 10) for lower elevation streams with a pH < 6.0 (Table 24). It could also reflect greater acid sensitivity of YOY rainbow trout compared to adults. These results compare with the Kendall's tau correlation analysis in Table 21. Metrics for sympatric brook trout were significantly greater in streams with a pH > 6.0 than where pH < 6.0; metrics included YOY density and biomass, and adult condition factor K (p = 0.02, 0.01, and < 0.01, respectively) (Table 24). All six metrics for sympatric rainbow trout were

significantly greater in streams with pH < 6.0 (p < 0.01). Competitive interactions may be influencing the brook trout results, where rainbow trout results may reflect differences solely due to acidification impairment. Rainbow trout populations are considered competitively dominant over brook trout (Larson et al. 1995). The Section 7.2.3 analysis also found that statistics may be influenced by trout competitive interaction coupled with the stream pH-elevation gradient. Overall, these statistics suggest a pH of 6.0 is a reasonable impairment threshold for both brook and rainbow trout.

7.4.3 Results: Acidity Effects on Macroinvertebrates

Several macroinvertebrate metrics were significantly greater in streams with a pH > 6.0 than

where $\text{pH} < 6.0$; which included EPT richness, taxa richness and abundance, richness of all functional feeding groups, scraper abundance, and bioclassification (Table 25). Two macroinvertebrate metrics, NCBI and shredder abundance, were significantly less in streams with a $\text{pH} > 6.0$ than where $\text{pH} < 6.0$. Although this analysis may include covariance of a pH elevation trend with richness, numbers of species (richness) were less when stream pH was below 6.0. Statistical analyses along elevation bands were not performed because data numbers were limited (Fig. 6). Bioclassification scores were significantly greater in streams with a $\text{pH} > 6.0$, suggesting better biotic integrity in those streams compared to streams with a $\text{pH} < 6.0$. However, it must be noted that both scores for $<$ and $>$ pH 6.0 were classified as good to excellent condition; therefore, macroinvertebrate communities may be impacted by stream acidity, but conditions do not lead to impairment.

7.5 Biotic Interactions

7.5.1 Objective and methods: biotic interactions

Exploratory analyses were conducted to identify related biotic metrics between trout and macroinvertebrates, and between brook and rainbow trout. The objective for examining the data for relationships was to assess whether trout populations may be affected by limitations on food resources, and to assess the influence of interspecific competition. The main objective was to determine whether there is some value in exploring this question in future research efforts. A Kendall's tau correlation analysis was used for both analyses using JMP software. Collocated data were used as defined in Section 2.2.4. A complete set of correlation coefficients from this analysis is in Appendix 13.

7.5.2 Results: Relationships between Macroinvertebrate and Trout Metrics

YOY and adult brook trout were not significantly correlated with the macroinvertebrate metrics, except for NCBI (Table 26). Density and biomass, for both YOY and adult brook trout, were inversely correlated with NCBI, inferring that brook trout populations were smaller in streams with more of the tolerant species of macroinvertebrates ($p < 0.05$); however, the result could be due to covariance between NCBI and elevation (Table 12). YOY brook trout were directly correlated with shredder richness, indicating a possible relationship between brook trout and food availability.

In general, macroinvertebrate metrics correlated more frequently with rainbow trout metrics than with brook trout metrics (Table 26). Density and biomass, for both YOY and adult rainbow trout, were directly correlated with taxa richness, richness of collector-filterers and collector-gatherers, and scraper abundance. YOY rainbow trout biomass was directly correlated with richness of scrapers and shredders, and inversely correlated with EPT abundance. Adult density and biomass were directly correlated with EPT richness and collector-filterer abundance, and inversely correlated with predator abundance. Results indicate that availability of food resources could be one factor in governing rainbow trout populations, but interactions with stream acidification cannot be made with the available data.

7.5.3 Results: Relationships between Brook and Rainbow Trout Metrics

An exploratory analysis was conducted to identify relationships between brook and rainbow trout metrics, as an indicator of potential competitive interactions between the two trout species. In order to complete this analysis, only fish survey sites containing sympatric populations were considered. Sites with sympatric populations were found along a similar elevation band, thereby

reducing the statistical effect of elevation gradient. A complete set of correlation coefficients from this analysis is in Appendix 14.

Adult brook trout density and biomass were inversely correlated with adult and YOY rainbow trout density and biomass (Table 27). Correlation coefficients (r) ranged from -0.25 to -0.46. YOY brook trout density was found to be inversely correlated with YOY and adult rainbow trout biomass. These results potentially indicate an effect of competitive interactions between the trout species, and an interaction with acidification may be occurring (Section 7.4.2). Effects of stream acidity on rainbow trout appear to be statistically stronger than with brook trout (Table 24). Within mid-elevation streams, where sympatric populations dominantly occur, statistics infer that brook trout populations may be more affected by the presence of rainbow trout than by the effects of stream acidification. The reverse may be true for rainbow trout, where acidification effects dominate over interspecific competition.

Table 27. Correlation coefficients between YOY and adult brook and rainbow trout using a Kendall's tau correlation analysis. Significant correlations shown were $p < 0.05$.

			Rainbow Trout					
			YOY			Adult		
			Density	Biomass	K	Density	Biomass	K
Brook Trout	YOY	Density		-0.20	-0.18		-0.18	
		Biomass						
		K			0.32			
	Adult	Density	-0.37	-0.44	-0.29	-0.25	-0.30	
		Biomass	-0.40	-0.46	-0.26	-0.28	-0.31	
		K	-0.23	-0.24		-0.21	-0.19	0.21

8.0 Summary and Discussion

Water quality, fish and benthic macroinvertebrate data collected from the period 1990 through 2009 in GRSM was statistically analyzed for potential biological effects from acid deposition. Stream acidification occurs in GRSM from acid deposition and the park's base-poor geology. However, the degree of acidification varies by watershed and its characteristics, including basin size and elevation, exposed pyritic Anakeesta rock, soil properties, vegetative cover, and disturbance history (Neff et al. 2013). Because of the variability in acidification response by watershed, relating basin factors with stream water quality provides key information to identify what watersheds and areas may be more prone to acid deposition. To assess biological effects, water quality per individual stream site had to be compared with chemistry-based toxicological thresholds to quantify exceedances. Because data have been collected over an extended period of time, a central management question for GRSM was to assess whether water quality conditions associated with acidic deposition are improving or degrading. In order to comprehensively address these questions, a statistical analysis of GRSM datasets was organized by four major efforts:

1. Identify toxicological criteria of water quality for biological impairment from stream acidification;
2. Assess changes in stream acidification condition over time for stream water chemistry and aquatic biota metrics;
3. Relate watershed characteristics spatially with stream chemistry and aquatic biota metrics; and
4. Identify interrelationships among watershed characteristics, stream chemistry, and aquatic biota metrics associated with impairment conditions from stream acidification.

A summary of statistical results addressing these four major efforts is in Table 28. Recall, the long-term monitoring databases included a total of 387 stream survey sites for water quality, 298 for fish, and 118 for macroinvertebrates. A total of 75 collocated pairs were identified spatially, including 23 with matched water quality, fish, and macroinvertebrates, 24 with water quality and fish, 20 with water quality and macroinvertebrates, and eight with fish and macroinvertebrates (Section 2.2.4). Most survey measurements did not overlap in location or period collected, which limited the statistical methods that could be applied. Nonetheless, a comprehensive review of the three datasets yielded valuable information to meet the study's objectives.

Relevant to GRSM and stream acidification, toxicological thresholds for trout and other aquatic biota primarily included pH and dissolved aluminum, but dissolved zinc and other metals were also reported (Table 8, Appendix 10). Ion regulation on trout gill structures can be disrupted from high concentrations of monomeric aluminum (Al_{IM}) and/or protons (low pH) causing severe deficiency of extracellular sodium and other ions leading to death (Neville and Campbell 1988, Spry and Weiner 1991, Hermann et al. 1993, Courtney and Clements 1998). Because GRSM water quality data consisted of total dissolved aluminum (Al_{TOT} or Al) and not Al_{IM} , the PHREEQC model was used to estimate Al_{IM} concentrations from measured Al in order to assess whether Al_{TOT} could be used as a surrogate for Al_{IM} (Section 2.4.3). It was found from the model that 96% of Al_{TOT} was Al_{IM} , inferring that Al_{TOT} can be used as a surrogate for Al_{IM} in this

Table 28. Report summary of study objectives, statistical tests performed, and key results analyzing legacy water quality, fish, and benthic macroinvertebrate data in GRSM.

Study Objective	Analysis/Statistical Tests	Key Results
Identify toxicological criteria of water quality for biological impairment from stream acidification.	Literature review	Chemical parameters of concern include: pH, dissolved aluminum, and dissolved zinc. Regulatory defined impairment for pH is defined as < 6.0 . A biotic integrity regulatory target for ANC is $> 50 \mu\text{eq L}^{-1}$, and acidic condition is $< 0 \mu\text{eq L}^{-1}$. Toxic levels for pH include: < 6.0 = reduced trout growth and < 5.0 = potential for trout mortality; Al_{TOT} and Zn thresholds are > 0.2 and $> 0.219 \text{ mg L}^{-1}$, respectively.
	Chemistry analyses	PHREEQC models indicate that most dissolved aluminum is in the most toxic monomeric form when $\text{pH} < 6.0$. Most GRSM samples have a $\text{pH} < 6.0$, thus, dissolved Al is a reasonable surrogate for Al_{IM} . When $\text{BCS} > 50 \mu\text{eq L}^{-1}$, $\text{Al}_{\text{IM}} = 0$. When $\text{pH} < 5$, $\text{ANC} < 0 \mu\text{eq L}^{-1}$ and $\text{Al} > 0.20 \text{ mg L}^{-1}$.
	Scatterplots between water chemistry and trout abundance	No brook trout were collected below a stream pH of 5.5, and no rainbow trout below pH 5.8. No brook or rainbow trout collected below $\text{ANC} < 0 \mu\text{eq L}^{-1}$. Contrary to literature, GRSM data indicated aluminum toxicity thresholds for adult brook trout to be about $0.08\text{-}0.09 \text{ mg L}^{-1}$, and rainbow trout 0.13 mg L^{-1} . Brook trout density is optimal when $\text{BCS} > 50 \mu\text{eq L}^{-1}$. When $\text{SO}_4^{2-} > 35 \mu\text{eq L}^{-1}$, brook trout density appears to decline; noting that dissolved Al co-varied with SO_4^{2-} and H^+ .
	GIS spatial analysis	Based on current data (2003-2009), stream sites with pH below 5.5 and ANC below $50 \mu\text{eq L}^{-1}$ occurred at higher elevations above 3500 ft (1067 m), except for streams in the Cosby Creek watershed. Based on all data (1993-2009), 51 sites had a $\text{pH} < 6.0$, and 13 sites had a $\text{pH} < 5.0$. All sites with $\text{pH} < 5.0$ were above an elevation of 4200 ft (1372 m).

Study Objective	Analysis/Statistical Tests	Key Results
<p>Assess changes in stream acidification condition over time for stream water chemistry and aquatic biota metrics.</p>	<p>Linear regression models using Julian date as the independent variable. Time period assessed = 1993 to 2009.</p>	<p>Summary of time trends among the 92 sites (number of sites per parameter): pH, ANC = 67 ↔; 21 ↑ 4 ↓ Cl⁻ = 60 ↔; 19 ↑ 13 ↓ SO₄²⁻ = 60 ↔; 18 ↑ 14 ↓ NO₃⁻ = 55 ↔; 25 ↑ 12 ↓ Ca²⁺ = 71 ↔; 20 ↑ 1 ↓ Mg²⁺, Na⁺, K⁺ = 64 ↔; 23 ↑ 5 ↓ Al = 81 ↔; 1 ↑ 10 ↓</p> <p>Over the long term, water quality parameters remained statistically unchanged for most stream sites; however, nitrate increased in 27.2% of the total 92 sites assessed, more than any other parameter.</p> <p>ANC and pH increased in 22.8% of the total 92 sites assessed. Many of these sites also were observed with increasing acid anions; thus, ANC and pH increases were primarily due to increasing base cations (Ca²⁺, Mg²⁺, Na⁺, K⁺). Dissolved Al was found to be declining in 10 sites, and increasing in only one site among the 92 sites assessed.</p> <p>ANC and pH declined in four sites in the Cosby Creek watershed, where acidic anions increased and base cations showed no trend, possibly indicating soils depleted of base cations. Rock Creek was also observed with declining trout population metrics.</p> <p>Brook trout population metrics increased over time in four sites (of 40 collocated sites) with increasing stream pH. Rainbow trout population metrics decreased over time in 12 sites, and increased in three sites, where relationships with water quality parameters were not consistent.</p>

Study Objective	Analysis/Statistical Tests	Key Results
Relate watershed characteristics spatially with stream chemistry and aquatic biotic metrics.	Linear regression models	<p>With an increase in elevation (\uparrow), the following chemical parameters and biotic metrics changed as follow:</p> <p>\downarrow = pH, ANC, conductivity, Cl^-, Ca^{2+}, Mg^{2+}, Na^+, K^+</p> <p>\leftrightarrow = SO_4^{2-}</p> <p>\uparrow = NO_3^-</p> <p>\uparrow = BKT adult and YOY, density and biomass</p> <p>\downarrow = RBT adult and YOY, density and biomass</p> <p>\downarrow = NCBI, EPT richness, taxa richness and abundance</p> <p>\downarrow = Collector-filter richness and abundance</p> <p>\downarrow = Collector-gatherer, predator, and scraper richness</p> <p>\uparrow = EPT abundance, shredder abundance</p>
	ANOVA Tukey HSD means separation analysis for elevation and sulfate concentrations for different time periods.	<p>Significant increases were seen in $[\text{SO}_4^{2-}]$ between 1993-2003 and 1993-2009 for elevation bands 3000 ft (914 m) - 4000 ft (1219 m) and 4000 ft - 5000 ft (1524 m), but not at lower elevations, inferring the possibility of soil desorption and transport to streams in later years concurrent with reductions in sulfate deposition; however, sample numbers were low and inferences should be considered speculative.</p>
	ANOVA Tukey-Kramer means separation analysis for baseflow and stormflow chemistry in eight-block design basins (Neff et al. 2013).	<p>Stream chemistry differed between baseflow and stormflow stages; during stormflows pH \downarrow and Al \uparrow.</p> <p>During baseflow, in high vs low elevation basins, pH, ANC, Na^+ \downarrow and NO_3^- \uparrow</p> <p>During stormflows in streams with Anakeesta geology, pH, Na^+ \downarrow and Al \uparrow, but not during baseflows.</p> <p>Soil and vegetation overstory characteristics strongly influenced both baseflow and stormflow chemistries.</p>

Study Objective	Analysis/Statistical Tests	Key Results
	Spearman correlation analysis (Neff et al. 2013).	Soil hydraulic conductivity (Ksat) ↑ = stream pH, ANC, base cations ↓ ; SO_4^{2-} , NO_3^- , Al ↑
	ANOVA single factor analysis and Tukey HSD means separation analysis for biotic metrics within eight-block design watersheds.	<p>In smaller subwatersheds, adult BKT density and biomass ↓ ; for example, in Rock Creek compared to Road Prong and Lost Bottom Creek, although lower in elevation.</p> <p>In larger watersheds with sympatric trout populations, BKT density and biomass ↑ ; for example, in Palmer Creek compared with Cosby Creek and Walker Camp Prong. Jakes Creek had the greatest RBT density and biomass.</p> <p>Macroinvertebrate index scores indicate streams in good to excellent condition overall. Although good, NCBI scores indicate poorer condition in Cosby Creek watershed compared to other watersheds.</p>
Identify interrelationships among watershed characteristics, stream chemistry, and aquatic biota metrics associated with impairment conditions from stream acidification.	Stepwise multiple regression models to relate watershed characteristics with water quality	<p>Average basin slope ↑ = ANC, BCS, Cl^-, K^+ ↓ ; SO_4^{2-}, NO_3^-, Ca^{2+} ↑ Elevation ↑ = ANC, Mg^{2+} ↓ % area Anakeesta ↑ = pH, BCS, Ca^{2+}, K^+ ↓ ; SO_4^{2-}, Cl^-, Mg^{2+} ↑</p> <p>Various forest cover types were selected secondarily in all regression models. Also, BCS ↓ with ↑ Humic-Typic_Dystrudepts soil.</p> <p>Stream acidification was related to steeper-sloped watersheds, likely due to increased sulfate and nitrate deposition in higher elevation areas, and some interrelationships with the presence of Anakeesta geology.</p> <p>Some indication that calcium is being exported from watersheds due to soil acidification, but not depleted overall among GRSM streams. Note, other data indicates Rock Creek watershed may be</p>

Study Objective	Analysis/Statistical Tests	Key Results
		Ca^{2+} depleted.
	Structural equations models (SEMs) to relate watershed characteristics with water quality	<p>Elevation, soil hydraulic conductivity, spruce-fir forest \uparrow basin area \downarrow related to $\uparrow \text{NO}_3^-$ and $\downarrow \text{pH}$, Na^+, K^+</p> <p>Stream acidification in high elevation, smaller basins with spruce-fir vegetation, and high soil hydraulic conductivity (steep basin slope = surrogate) appears to be driven by nitrate, corresponding to lower sodium and potassium in streams.</p>
	Kendall's tau correlation analysis to relate water quality with biotic metrics	<p>For both sympatric and allopatric trout populations: pH, ANC, $\text{BCS} \downarrow = \text{BKT ADT} \uparrow$; RBT YOY and $\text{ADT} \downarrow$ $\text{SO}_4^{2+} \uparrow = \text{BKT YOY} \downarrow$; RBT YOY and $\text{ADT} \downarrow$ $\text{NO}_3^- \uparrow = \text{BKT YOY}$ and $\text{ADT} \uparrow$; RBT YOY and $\text{ADT} \downarrow$ $\text{AI} \uparrow = \text{RBT YOY} \downarrow$</p> <p>For allopatric trout populations only: pH, ANC, $\text{BCS} \downarrow = \text{BKT YOY}$ and $\text{ADT} \downarrow$; RBT YOY and $\text{ADT} \downarrow$ $\text{SO}_4^{2+} \uparrow = \text{BKT YOY}$ and $\text{ADT} \downarrow$; $\text{RBT YOY biomass} \downarrow$ $\text{NO}_3^- \uparrow = \text{BKT YOY biomass} \downarrow$; $\text{RBT YOY} \downarrow$ $\text{AI} \uparrow = \text{BKT YOY} \downarrow$</p> <p>Impacts of stream acidification were observed on brook and rainbow trout when allopatric population data was used, but not for brook trout when all data was used, suggesting that the analysis with all data was influenced by basin gradients in trout distribution and water quality.</p>
	Stepwise regression models to relate water quality with trout and macroinvertebrate metrics	<p>$\text{NO}_3^- \uparrow \text{SO}_4^{2+} \downarrow \text{K} \uparrow = \text{BKT ADT}$ and $\text{YOY density and biomass} \uparrow$ $\text{pH} \downarrow = \text{BKT YOY density and biomass} \uparrow$ $\text{K} \uparrow \text{BCS} \uparrow = \text{RBT YOY density and biomass} \uparrow$ $\text{NO}_3^- \downarrow \text{NH}_4^+ \uparrow = \text{RBT ADT density and biomass} \uparrow$</p>

Study Objective	Analysis/Statistical Tests	Key Results
		<p>pH or ANC \uparrow = TR, RSCR, RSHR, ASCR \uparrow SO_4^{2+} \uparrow = NCBI and ASCR \uparrow ; RCGA, RPRE, ACGA \downarrow NO_3^- \uparrow = RCFI and ACFI \downarrow Al \uparrow = EPTR and RSCR \downarrow</p> <p>Results for biotic metrics with pH and NO_3^- indicated an influence by elevation gradients, except for SO_4^{2+}, which inferred some acidification impacts on brook trout and intolerant macroinvertebrates.</p>
	Structural equation models (SEMs) to relate water quality with trout and macroinvertebrate metrics, separately	<p>Stream chemical parameters were similarly correlated for all three SEMs with trout and macroinvertebrate metrics. Increased biotic metrics were correlated with pH, ANC, Na^+, K^+ \uparrow and SO_4^{2+}, NO_3^- \downarrow</p> <p>Biotic metrics that correlated with stream chemistry included: BKT ADT and YOY; RBT ADT and YOY biomass and ADT K; and EPTR, TA, and TR.</p>
	Structural equation models (SEMs) to relate watershed, water quality, and trout metric variables	<p>pH, Na^+, K^+ \uparrow and NO_3^- \downarrow related to mean elevation, Ksat, and % cover of spruce fir \uparrow, and basin area \downarrow. These water quality parameters and watershed characteristics are related to BKT ADT and YOY K \uparrow, and RBT ADT and YOY biomass \uparrow</p>
	Student's t-test examining two acidity classes ($<$ and $>$ pH = 6.0) for biotic metrics in 303(d) listed streams	<p>Allopatric BKT \uparrow when pH $>$ 6: ADT and YOY density and biomass Allopatric RBT \uparrow when pH $>$ 6: YOY density and biomass Sympatric BKT \uparrow when pH $>$ 6: YOY density and biomass Sympatric RBT \uparrow when pH $>$ 6: ADT and YOY density and biomass</p>

Study Objective	Analysis/Statistical Tests	Key Results
		<p>Results indicate that brook trout are impacted by episodic stream acidification, and when occupied with rainbow trout as sympatric populations, there may be competitive interactions.</p> <p>When pH > 6; NCBI ↓ and BIOC ↑; EPTR, TR, TA, and all richness metrics among functional groups ↑; all indicate better stream conditions for macroinvertebrates.</p>
	Kendall's tau correlation analysis between trout and macroinvertebrate biotic metrics, and between brook and rainbow trout metrics.	<p>BKT YOY and ADT density and biomass ↑ = NCBI ↓ (better condition)</p> <p>BKT YOY and ADT density and biomass ↑ = RSHR ↑</p> <p>RBT YOY density and biomass ↑ = EPTA ↓; TR, RCFI, RCGA, RSCR, ASHR ↑</p> <p>RBT ADT density and biomass ↑ = APRE ↓; EPTR, BIOC, TR, RCFI, RCGA, and ASCR ↑</p> <p>BKT ADT density and biomass ↑ = RBT ADT and YOY density and biomass ↓</p>

study's toxicological assessment. Also, organic acid concentrations had to be assumed in the PHREEQC model, and estimates were made based on dissolved organic carbon (DOC) data from Deyton et al. (2009). Knowing DOC concentrations is important because elevated levels can reduce Al_{IM} toxicity (Driscoll 1985). DOC is not routinely analyzed in the current water quality monitoring program, and should be considered as a chemical parameter to be monitored for future efforts to better assess the potential of Al_{IM} toxicity.

With a focus on trout, toxicological thresholds included: 1) reduced growth below a pH of 6.0, and 2) increased risk for mortality below a pH of 5.0 and above an Al_{TOT} of 0.2 mg L^{-1} (Table 8). Baldigo et al. 2009 classified stream pH toxicity levels as: 1) pH 6.4 to 5.5 = slight impairment, 2) pH 5.5 to 5.0 = moderate impairment, 3) pH 5.0 to 4.0 = severe impairment, and 4) < 4.0 = lethal. State water quality standards for Tennessee and North Carolina require a pH in the range of 6.0 to 9.0. ANC is an acidity measure associated with pH, and used by TDEC for developing acidity TMDLs with a target of greater than $50 \text{ } \mu\text{eq L}^{-1}$. An ANC below $0 \text{ } \mu\text{eq L}^{-1}$ is generally classified as acidic water (Wigington et al. 1996a, 1996b).

Within the park-wide dataset for water quality (1993-2009), measured stream pH ranged from non-impaired to severely-impaired for both baseflow and stormflow conditions (Table 4). Among the 387 water quality sites sampled mostly during 1993-1995, median stream pH for baseflow was 6.63, but the minimum was 4.44. During baseflow, 47 sites were measured with a pH below 6.0, and 10 sites below pH 5.0. Median stormflow pH was 6.47 with a minimum of 4.39. During stormflow, 51 sites were found with a pH below 6.0, and 13 sites below a median pH of 5.0. About 13% of GRSM monitoring sites over the 16-year monitoring period were below the regulatory pH limit of 6.0, which provides a general idea of the extent of stream acidification across the park. With the current 43 sites sampled bimonthly, 10.8% of the 2011 samples were below pH 6.0, with one or more exceedances occurring within Cosby Creek, Road Prong, Oconaluftee River, and Cataloochee Creek watersheds (Schwartz et al. 2012).

A pH target of > 6.0 is justified by several analyses, with evidence supporting that stream pH levels near or above 6.0 will improve biological integrity in GRSM. By comparing trout density versus pH in scatterplots of collocated data (Figs. 10-13), maximum densities (fish per 100 m^2) for YOY and adult brook and rainbow trout occurred when pH was above 6.0, and optimal densities occurred when pH was above 6.5. No brook and rainbow trout were collected in streams with pH lower than 5.5 and 5.8, respectively. Correspondingly, no trout were collected in streams with an ANC below $0 \text{ } \mu\text{eq L}^{-1}$. Per allopatric populations, reduced YOY and adult densities and biomass for both brook and rainbow trout were statistically correlated with lower pH and ANC (Table 21). Providing evidence that the pH 6.0 target has biological relevance, brook and rainbow trout biotic metrics were statistically different for streams with a pH above and below 6.0 (Table 24). Macroinvertebrate metrics were also statistically different in streams with a pH above and below 6.0. Although macroinvertebrate metrics were not considered as impaired for both pH classes when stream pH levels were above 6.0, metrics did infer improved biological integrity, which included all functional group richness metrics, taxa abundance, and NCBI (Table 25).

Within the entire water quality dataset, median Al_{TOT} was 0.04 mg L^{-1} for baseflow and stormflow conditions (Table 4), which was below the toxicological threshold of 0.2 mg L^{-1} . Maximum reported concentrations were 0.45 and 0.41 mg L^{-1} , respectively for baseflow and

stormflow conditions, both exceeding the toxicological threshold. Although the literature reported a threshold of 0.2 mg L^{-1} , no adult brook trout were found in streams with an Al_{TOT} above 0.09 mg L^{-1} , and no adult rainbow trout were found with values above 0.13 mg L^{-1} (Figs. 10-13). These two observed thresholds may be a more relevant Al concentration threshold for GRSM streams during baseflow conditions. Higher Al thresholds in the literature for trout were likely due to their experimental designs utilizing laboratory procedures. Acute exposures during laboratory experiments more represent short-term stormflow conditions rather than long-term baseflow stream chemistry. In this study, elevated Al concentrations were inversely correlated with pH during stormflow but not baseflow, inferring that increased exposure concentrations occurred during stormflows. In other words, streams in the range of $0.08\text{-}0.09 \text{ mg L}^{-1}$ during baseflow, likely exceeded 0.2 mg L^{-1} during stormflow. Neff et al. (2009) observed this shift in increased Al_{TOT} from baseflow to stormflow.

Spatially within GRSM, six sites had a median Al concentration above 0.2 mg L^{-1} and 24 sites were above 0.087 mg L^{-1} , representing about 6% of the survey sites (Fig. 16). Although the number of survey sites exceeding an Al toxicological threshold was low, statistical evidence suggest in-stream Al concentration may affect allopatric YOY brook trout based on a significant inverse correlation (Table 21). Significant correlations were not observed with adult brook and rainbow trout metrics within allopatric sites. These results suggest brook trout recruitment may be affected by a chronic acidity stressor on YOY. A range of trout life stages should also be considered when setting toxicity thresholds, where YOY may be more vulnerable than adults (Baldigo et al. 2009). Although the discussion has focused on trout impairment, reduced macroinvertebrate metrics, including EPT and scraper richness, were also statistically correlated with elevated aluminum concentrations (Table 20).

The source of dissolved Al in streams is from soil dissolution when soil water pH is lowered, caused by acid deposition, and transported by shallow groundwater flow during rain events (Driscoll 1984, Postek et al. 1995, Lawrence 2002, Cai et al. 2011b). In acidic soils with pH below 4.5, Al_{TOT} will be the Al^{3+} monomeric form, and soil adsorption of sulfate is strongly promoted. This geochemical process is highly pH dependent. For example, when soil water pH is above 6.0, exchangeable aluminum will remain attached onto the soil particles and sulfate will desorb into water solution which then can be readily transported by shallow groundwater flow to nearby streams. A regression model developed in this study and used to predict Al_{TOT} was directly related to sulfate and proton concentrations (Section 2.4.1). This model was useful for estimating stream Al concentrations for years prior to 2003 in which dissolved metals were not analyzed. More importantly, the model related stream pH, sulfate, and Al_{TOT} , illustrating the dominant influence of soil biogeochemical processes on stream acidification dynamics. It also suggests that sulfate concentration could be used as a surrogate measure for Al toxicity, which is a conclusion supported by the scatterplot data where YOY brook trout densities declined above a SO_4^{2-} of $35 \text{ } \mu\text{eq L}^{-1}$ (Fig. 10). Also, as a function of exchangeable cation, and cation export from soils, stream chemistry and Al concentrations were related to BCS, where stream Al_{TOT} was always below detectable levels when BCS was above $50 \text{ } \mu\text{eq L}^{-1}$ (Section 2.4.2). Lawrence et al. (2009) has suggested that BCS can be used as a surrogate measure for in-stream aluminum. In general, surrogate measures for Al toxicity do provide additional means to assess the potential for biological impairment from acidification.

As noted with Al toxicity, threshold differences occur based on the end point, whether it is mortality or chronically-stressed populations, and baseflow versus episodic stormflow events. Because of the episodic nature of stormflow chemistry, toxicological thresholds must consider not only magnitude, but duration and frequency (Robinson and Roby 2005). Neff et al. (2009) characterized the episodic nature of stream acidification in three GRSM streams and found that brook trout became physiologically stressed during stormflow, as measured by whole-body sodium loss, but recovered within about a day of the episode. The study by Neff et al. (2009) illustrated that brook trout populations may not die acutely from acidification, but rather prolonged and greater frequency of stressful events may lead to reduced survival. It also possibly indicates that stream sodium concentrations enhance brook trout recovery after episodic Al peaks during storm events (Neff 2010). Over the long term, if stressed environments persist in streams episodically, brook trout distribution could be impacted in GRSM (Mauney 2009). Others have noted the potential long-term sub-lethal impacts on trout populations from episodic acidification during stormflow events (Gagen et al. 1993, Baker et al. 1996, Baldigo et al. 2007). Overall, more study is needed considering toxicological responses to YOY trout and episodic events, defined in terms of magnitude-duration-frequency and ecological end-points other than acute trout mortality.

Locations of stream survey sites that exceeded toxicological thresholds for pH, ANC, and Al_{TOT} were mapped in order to identify biologically sensitive areas in GRSM, and most sensitive sites were found to occur at higher elevations (Figs. 14-16). Noting that the higher elevation streams above 4000 ft (1219 m) receive the highest loadings of acid deposition (Weathers et al. 2006), it was not unexpected that these streams were significantly lower in pH and ANC. Within GRSM, this study found stream pH and ANC to significantly decrease at -0.32 units and $-35.73 \mu eq L^{-1}$ respectively, per 1000-ft (305 m) elevation gain (Table 12). Streams with severe acidification with pH below 5.0 were located above 4200 ft (1280 m) elevation (Table 5). Stream sites with pH below 5.5 were located above 3500 ft (1067 m), except for the Cosby-Rock Creek watershed. It appears stream acidification in the lower elevation reaches of Rock and Cosby Creeks may be due to soil calcium depletion (Grell 2010), and increased nitrate export (Figs. 19-21). Overall, elevation is a dominant watershed characteristic that is significantly related to stream chemistry in GRSM (Section 6.1, Fig. 23), and others have also observed this elevation trend in the Appalachian region (Hyer et al. 1995, Sullivan et al. 2007).

Stream conductivity, chloride, and base cations were also found to significantly decrease with elevation gain. Inversely, stream nitrate significantly increased $8.42 \mu eq L^{-1}$ per 1000-ft elevation gain. Stream sulfate showed no significant trend with elevation. From a park-wide perspective, lower pH and ANC in the high-elevation headwater streams appear to be due to higher nitrate concentrations and lower base cations compared with lower elevation streams and rivers. Although sulfate deposition does contribute to stream acidity, from a longitudinal gradient perspective, in-stream concentrations remained constant. Consistent with the regression models, dominant basin factors determined by an SEM found that higher elevations correlated with lower pH, sodium, and potassium, and greater nitrate concentrations (Fig. 23). Other than elevation, the SEM correlated these stream chemistries with smaller basin areas, increased soil hydraulic conductivity, and spruce-fir forest cover. Collectively, these relationships and knowledge of governing biogeochemical processes were used to explain the longitudinal patterns in water quality along an elevation gradient.

Higher nitrate concentrations in the headwaters were likely due to high levels of atmospheric deposition (Weathers et al. 2006), rapid mobility through soils (Mulholland 1993), and forests determined to be at stage 2 nitrogen saturation (Van Miegroet et al. 2001). Stage 2 nitrogen saturation refers to forests that cannot assimilate all of the available incoming nitrogen, and nitrogen as nitrate dominates export to the stream. Ammonia nitrogen that is deposited from atmospheric sources is rapidly converted to nitrate by soil mineralization and nitrification, and these biochemical processes appear to increase with elevation, adding to the stage 2 nitrogen saturation (Cai et al. 2011a, Rolison 2012). Cai et al. (2010) quantified the net nitrogen export from the Noland Divide watershed, a high-elevation GRSM site. Although it appears that stage 2 nitrogen saturation prevails among the high-elevation watersheds, each watershed has unique uptake rates due to forest composition and condition. For example, watersheds with excessive hemlock die-off from the balsam woolly adelgid would be expected to export nitrate to streams differently than watersheds with dense canopy deciduous forests. Regression models did find that forest cover types were significantly related to stream nitrate (Table 18, Fig. 23). In addition, Deyton et al. (2009) found that in-stream nitrate concentrations varied seasonally, where nitrate was greater during leaf-off months than during leaf-on months, illustrating the influence of forest uptake rates on nitrogen export. Explanations for lower nitrate concentrations among the low-elevation streams are likely due to less deposition (Weathers et al. 2006), and stream uptake by periphyton, biofilm, and riparian plants with downstream flow from the higher elevation headwaters (Mulholland 2004).

Base cation concentrations increased from headwater streams to lower elevation streams and rivers, likely as a function of soil/rock weathering and ion accumulation with groundwater transport (McKenna 2007). In the headwaters, basin slope is steep and rainwater entering the soil moves quickly through shallow horizons, as evidenced by the greater soil hydraulic conductivity (Fig. 23). Mulholland (1993) reports a portion of the soil water exits to the headwater stream while a portion enters deeper geological layers. Water that enters deeper fractured rock and is transported by groundwater flow has longer contact time with fractured rock compared to its transport in upper headwater and soil systems. Base cation dissolution from weathering increases in groundwater with longer exposure times. Lower elevation streams and rivers have more groundwater inputs, and would be expected to be greater in base cation concentrations due to this water being exposed longer to subterranean rock (Table 12). Base cation concentrations were not significantly different between baseflow and stormflow (Table 4), which indicates regulation of stream base cations by groundwater transport. Deyton et al. (2009) found that episodic stream acidification was rarely due to base cation dilution, which also indicates that groundwater flow regulates cation transport in the lower elevation streams and rivers.

Stream acidification can occur when soils and geological sources become depleted of base cations reducing a stream's acid buffering capacity. In northern Appalachian streams, acidification from soil calcium depletion has been documented (Mitchell et al. 1992, Fernandez et al. 2003). Among GRSM streams, base cation depletion from soils does not appear to occur to any park-wide extent, but possibly occurs in one watershed (Cosby Creek). In this watershed, low pH and ANC appeared to be due to a lack of cations to buffer increased acidity from nitrate. In addition to calcium, sodium and potassium are generally known to be controlled by forest-soil dynamics, where transport from land to streams is governed by vegetation uptake and release (Ferm and Hultberg 1999, Oyarzún et al. 2004). SEM statistics found that stream sodium and potassium concentrations were significantly less at higher elevations, which may be attributed to

forest nutrient cycling. In the Noland Divide watershed, Cai et al. (2010) found that 71% of potassium was retained from 1991-2006, but a net sodium flux was exported by 18%. Reduced potassium concentrations were likely due to retention in the forest biomass. Differences in forest cover type will regulate cation retention or export differently, so other watersheds will likely vary from what was reported at Noland Divide. Overall, forest-soil cycling of cations, nitrogen, and organic matter are fundamental processes that regulate ion export to streams, and thus stream water quality (Johnson and Lindberg 1992).

Stream sulfate was not strongly influenced by elevation, indicating that other basin factors control its concentrations. The source of stream sulfate is mostly from atmospheric deposition, although Anakeesta pyritic geology can be a potential source when it is exposed to rain. In the eight-block design study, watersheds with greater than 10% land area of Anakeesta were significantly correlated with stream sulfate during stormflow but not baseflow (Neff et al. 2013). Anakeesta was also found to be a significant watershed independent variable in the logistic regression model for sulfate using the collocated water quality and trout survey sites; however, basin slope was the most significant variable (Table 18). In other applied statistics, increased basin slope was related to increased soil hydraulic conductivity, which suggests that sulfate transport to streams may primarily occur with flow through saturated soils during rain periods. Zimmerman (2011) found this to be the case, but only for small headwater streams and not larger streams with watershed areas greater than 10 km². Overall, sulfate is largely controlled by soil adsorption processes (Mitchell 2001, Lawrence 2002, Cai et al. 2011a). From a park-wide perspective, it is reasonable to view soils as a sulfate export regulator where variable inputs are filtered and a constant concentration release is maintained over time for baseflow conditions. Observed variability with stream sulfate could be attributed to timing of sample collection with respect to stormflow and baseflow stage. In order to improve our understanding of sulfate transport dynamics, water monitoring should differentiate between baseflow and stormflow collections.

Elevation was significantly correlated with trout species distribution and macroinvertebrate metrics (Section 6.1, Fig. 26). While there were some exceptions, allopatric populations of brook trout were generally found in the higher elevation streams, allopatric rainbow trout were in the lower elevation streams, and sympatric populations were found at mid elevations (Fig. 17). Statistically, YOY and adult brook trout density and biomass increased with elevation gain, whereas rainbow trout metrics decreased (Table 12). Macroinvertebrate metrics, including EPT richness, taxa richness and abundance, and richness of all functional feeding groups except shredders, generally decreased with elevation gain. Because of these elevation trends with biotic metrics, applied statistics with water quality parameters and biotic metrics were influenced by collinearity. Therefore, significant relationships between these two sets of variables do not imply cause and effect, unless collinearity with elevation was addressed. Sulfate was the one water quality parameter without a significant elevation trend, thus greater credence can be given to significant relationships associated with potential impacts from acidification. Overall, this finding suggests that future monitoring designs in GRSM should include sufficient numbers of sites along common elevation bands.

Spatial relationships among watershed characteristics, stream water chemistry, and biotic metrics were completed with data ranging from 1993 through 2009; thus, a key question to address was whether water quality data were changing over this monitoring period. Not only was this trend

analysis needed to justify the observed spatial statistics with elevation, it was important to know whether water quality has been improving or degrading over time in GRSM. Overall, the park-wide stream chemistries remained mostly unchanged over the 1993-2009 period. Among the 92 stream sites assessed, unchanged sites ranged from a low of 55 for nitrate to a high of 81 for dissolved Al (Table 28). In the case for stream acidity, 67 sites were statistically constant, while 22 survey sites had increased (improved) pH at a rate of 0.01-0.03 units per year (Tables 10, 11). Two sites, Rock and Cosby Creeks, were found to have decreasing pH at an annual rate of 0.03 units, which was noted before as due to increased nitrate and constant annual base cation concentrations.

Stream sites with observed annual increases in nitrate were distributed throughout the park (Fig. 20); therefore, the cause was likely from a widespread source. Two possibilities for this source include an overall increased level of nitrogen deposition and/or a greater availability of organic nitrogen from hemlock die-off and decay. NADP (2011) has reported increased nitrate and ammonium deposition nationally, including the southeastern US. Ammonium is converted to nitrate through mineralization and nitrification, and Rolison (2012) quantified nitrification rates along an elevation gradient in GRSM and determined that it is significant as a substantial nitrate source. Surface soil horizons are rich in organic matter, so any increases in ammonium will likely be rapidly converted to nitrate, and it appears that low-temperature winter periods have minimal effect on this microbial process at the higher elevations.

The 1993-2009 data generally support the conclusion that soil adsorption is a controlling geochemical process for sulfate export from watersheds, and that this process has been maintained by acid deposition and low soil pH. Cai et al. (2010) found that in the Noland Divide watershed, 61% of the atmospheric-deposited sulfate was retained in the soil. However, in the more recent years, sulfate deposition has declined among higher elevation watersheds, and this improvement could lead to greater sulfate export from the legacy retention, leading to increased stream sulfate (Schwartz et al. 2012). Cai et al. (2011a, 2012) determined that soil desorption, a rapid release of sulfate from the soil to the streams, is possible if soil water pH increases to above 6.0 and if sulfate drops below $50 \mu\text{eq L}^{-1}$. Some evidence suggests that stream sulfate levels among the water quality monitoring sites above 3000 ft (914 m) have increased with time (Table 13); however, some low elevation sites also show increased sulfate trends (Fig. 20). Sample numbers were small at the higher elevations; therefore, in order to thoroughly investigate whether excess sulfate export may be occurring from stored soil sulfate, more study is highly recommended.

Temporal changes with increased base cations predominantly occurred among high-elevation sites (Fig. 21). In contrast, decreased dissolved aluminum occurred among lower elevation sites. These two trends can be considered as improved conditions for water quality, although there were a small number of sites with temporal changes. Interpretation of these results indicates that GRSM soils have not been exhausted of their exchangeable cations. In general, soils analysis by Grell (2010) indicated that there is an ample supply of exchangeable soil cations. Because of the apparent source of base cations for GRSM streams, it appears that cation dilution will not be a controlling factor in stream acidification in the near future.

Co-varying relationships between water quality data and trout metrics were not evident from the temporal data analysis (Table 11). Only four of 40 collocated stream sites were observed with

significant increases in both pH and brook trout density and biomass. Macroinvertebrate data lacked sufficient samples to statistically conduct a temporal analysis. Because of the natural variability from other factors, such as hydrology (Parker 2008), longer term monitoring data will be required to adequately analyze time series for water quality parameters and trout metrics.

In summary, findings from this comprehensive data analysis provided valuable information on the relationships between watershed characteristics, water quality, and aquatic biota. Results will guide study site selection for GRSM's Vital Signs monitoring program, currently under development by the National Park Service natural resource staff. Coordinated site selection at the higher elevations will greatly improve future analyses assessing the impacts of acid deposition and stream acidification on GRSM's aquatic biota.

9.0 Data Limitations and Monitoring Recommendations

As stated in the *Summary and Discussion*, statistical analyses were limited by water quality, fish, and macroinvertebrate sites not collocated spatially nor sampled during the same time period. In addition, variable sample frequencies within and between the three monitoring efforts limited what statistics could be used for the temporal trend analysis. Collocated stream survey sites and a consistent sampling frequency over the long term would expand the types of statistical procedures that could be performed in the future and improve overall statistical power. For example, with collocated long-term data, time series analysis could be conducted estimating covariances among water quality and biotic metrics. In order to complete a time series analysis, biological survey sites should be monitored minimally on an annual basis without missing years. Because of the seasonal influences on water quality related to episodic stream acidification as reported by Deyton et al. 2009, water quality monitoring frequency should be conducted as least on a quarterly basis.

Water quality data collected along a longitudinal gradient from high-elevation headwaters to lower elevation rivers is recommended in order to interpret how biogeochemical processes influence the fate and transport of acid pollutants from atmospheric deposition. Monitoring water quality in headwater streams is very important with respect to understanding these processes because forest nutrient cycling and soil sorption properties appear to control nitrate, sulfate, and base cation concentrations. It is the chemical charge balance that determines stream water pH and ANC. A monitoring program design should include forest cover and condition, and soil physical and chemical properties including hydraulic conductivity and organic matter content.

Because of the strong longitudinal elevation gradients with water chemistry and aquatic biota, a monitoring design should consist of field sites selected in different watersheds among specified elevation ranges to reduce collinearity effects observed with this study's datasets. Sufficient numbers of sample sites among each elevation range are needed to provide adequate statistical power for analysis. Elevation ranges on a 1000-ft interval appear to be adequate; however, Robinson et al. (2008) used 500-ft intervals and that level of detail was useful in their analysis of acidification effects in GRSM. One possible set of elevation bands for monitoring is as follows: 1500-2500 ft (457-762 m), 2500-3500 ft (762-1067 m), 3500-4000 ft (1067-1219 m), 4000-4500 ft (1219-1372 m), 4500-5000 ft (1372-1524 m), and > 5000 ft (1524 m). Among the higher elevation sites, presence or absence of surficial Anakeesta geology and whether allopatric or sympatric brook trout populations reside in the stream should be considerations in site selection.

Differences in baseflow and stormflow chemistry were reported in this study, and reflect how sulfate, nitrate, and base cations are transported within the watersheds and exported by streams. Baseflow chemistry appeared to be influenced more by nitrate and base cations, whereas stormflow chemistry appeared to be more influenced by sulfate than the other ions. During stormflow, stream pH and ANC drop and dissolved aluminum concentrations rise episodically, and Neff et al. (2009) found that these episodic acidification events caused sublethal stress responses in GRSM brook trout. Sampling stormflow events is problematic, requiring more effort than baseflow sampling programs. Neff et al. (2013) effectively used passive sampling devices, and these devices could be considered for a number of sites among selected elevation bands and/or a watershed longitudinal gradient. Within the context of baseflow and stormflow stages, estimates of stream discharge would provide valuable hydrological information and allow

for more accurate chemical mass transport calculations. Parker (2008) did provide some evidence that trout populations are affected by drought and floods, and having stream discharge data would be useful for future analyses related to climate change impacts on GRSM's natural resources.

The current suite of chemical parameters monitored was valuable in conducting the toxicological assessment, and interpretation of watershed biogeochemical processes. Dissolved aluminum is an essential metal that needs to be monitored for any future toxicity assessments. Analyzing the water samples for DOC, as a surrogate for organic acids, would better support chemical modeling of aluminum speciation to estimate concentrations of inorganic monomeric aluminum (Al_{IM}). Direct laboratory analysis of Al_{IM} could also be conducted for future analysis, but due to the difficulty of laboratory procedure it would not be recommended for all samples.

A summary of possible improvements to the water quality monitoring program includes: 1) collocate water quality, fish, and macroinvertebrate stream sites, and sub-watershed forest and soil study sites; 2) focus on monitoring a statistically adequate number of stream sites above 3500 ft (1067 m) elevation; 3) add DOC to the suite of chemical parameters analyzed; 4) in addition to baseflow collections, collect stormwater samples in order to characterize chemical ion transport during elevated flow stages; and 5) estimate stream discharges at study sites.

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Appendix 1. Stream Survey Sites for Water Quality Monitoring: Descriptions and Locations.

Site ID	Site Description	Elev. (ft)	Stream Order	Longitude	Latitude	Survey period
1	Indian Camp at Old Settlers Trail	2200	3	-83.2777	35.75645	1993-2003
2	Dunns Creek at boundary	1990	4	-83.2858	35.76687	1994-1995
3	Cosby Creek at boundary	1675	4	-83.2185	35.78341	1993-2003
4	Lower Rock Creek	1680	3	-83.2172	35.78114	1993-2009
5	Cosby Creek at campground	2300	3	-83.2074	35.75523	1994-1996
6	Big Creek at campground	1715	4	-83.1094	35.75049	1993-1996
7	Chestnut Creek at ranger station	1710	4	-83.1084	35.75477	1994-1996
8	Hesse Creek at Rich Mountain Road	2060	2	-83.805	35.6373	1995-1996
9	Shell Branch (Hesse Creek)	2060	1	-83.8195	35.64958	1995-1996
10	Hesse Creek at Campsite 3	1480	4	-83.8458	35.66361	1995-1996
11	Lower Beard Cane Creek	1520	2	-83.8515	35.66008	1995-1996
12	Hesse Creek at old shelter	3300	1	-83.7887	35.63109	1995-1996
13	Little River at boundary	1100	5	-83.713	35.66586	1993-2009
14	Little River above Y	1140	4	-83.707	35.66006	1993-2003
15	Whiteoak Flats Branch (Little River)	1200	1	-83.7018	35.65919	1995-1996
16	Little River below first bridge	1300	4	-83.6851	35.66681	1993-1996
17	Little River at Sinks	1550	4	-83.6627	35.6697	1993-1996
18	Lower Meigs Creek	1680	3	-83.6593	35.65975	1995-1996
19	Little River (below Sinks and Metcalf Bottoms)	1600	4	-83.6587	35.67377	1993-1996
20	Little River at Metcalf Bottoms	1700	4	-83.6471	35.67844	1993-2003
21	Little Brier Branch at school	1790	2	-83.6385	35.68358	1993-1996
22	Upper Little Brier Branch	2000	2	-83.6317	35.6952	1995-1996
23	Lower Middle Prong Little River	1150	4	-83.7095	35.65726	1993-2006
24	Lower West Prong Little River	1150	3	-83.7103	35.65601	1993-2009
25	Laurel Creek at Schoolhouse Gap	1520	3	-83.7264	35.62791	1993-1996
26	LeConte Creek at boundary	1550	2	-83.5105	35.69936	1994-1996
27	Scratch Britches at Uplands	1950	1	-83.5008	35.68641	1994-1996
28	LeConte Creek at Uplands	1950	2	-83.5005	35.68655	1994-1996
29	West Prong Little Pigeon at boundary	1330	4	-83.5272	35.70121	1993-1996
30	West Prong Little Pigeon at Headquarters	1430	4	-83.5364	35.68813	1993-2009
31	West Prong Little Pigeon across from Husky Gap	1740	4	-83.5223	35.66465	1993-1996
32	Critter Brook (West Prong Little Pigeon)	2030	1	-83.5206	35.65768	1994-1996
33	Lower Big Branch (West Prong Little Pigeon)	2600	2	-83.5023	35.65604	1995-1995
34	Little River at Milsap Site	1990	4	-83.6038	35.66478	1993-2003
35	Little River at Elkmont Campground	2090	4	-83.5846	35.65951	1993-1995
36	Laurel Branch at Laurel Falls	2600	3	-83.5932	35.67741	1995-1996
37	Fighting Creek	1550	2	-83.5508	35.68037	1994-1996
38	Jakes Creek at cabins/trailhead	2320	2	-83.5831	35.6488	1993-1996
39	Middle Jakes Creek	3275	1	-83.5972	35.6282	1993-1996
40	Little River at old road gate	2300	4	-83.5633	35.64973	1993-1995
41	Husky Branch (Little River)	2500	2	-83.5517	35.63855	1993-1995

Site ID	Site Description	Elev. (ft)	Stream Order	Longitude	Latitude	Survey period
42	Little River at damaged bridge	2590	4	-83.5446	35.63339	1993-1995
43	Porters Creek at log bridge	2080	4	-83.3959	35.689	1993-2004
44	Upper Cannon Creek	3400	2	-83.4127	35.67228	1993-1995
45	Shutts Prong	3200	2	-83.3976	35.65906	1993-2003
46	Porters Creek above Shutts Prong	2750	3	-83.3959	35.66904	1994-2003
47	Lower Cannon Creek	2400	2	-83.3987	35.68027	1994-2003
48	Porters Creek at gate	1800	4	-83.3851	35.69876	1993-1996
49	Porters Creek at bridge to Ramsay	1650	4	-83.3826	35.70802	1993-2003
50	Middle Prong Little Pigeon below Porters	1600	5	-83.383	35.71418	1993-2003
51	Middle Prong Little Pigeon near ranger station	1470	5	-83.399	35.725	1993-1996
52	Middle Prong Little Pigeon at boundary	1350	5	-83.4162	35.73847	1993-2003
53	Surry Fork (Roaring Fork)	4435	1	-83.4372	35.66969	1993-1996
54	Roaring Fork at Grotto Falls	3680	1	-83.4499	35.67423	1993-1996
55	Unnamed tributary to Roaring Fork	3620	1	-83.4521	35.67615	1994-1996
56	Rocky Spur (Roaring Fork)	3410	1	-83.4541	35.67559	1993-1996
57	Roaring Fork at Grapeyard Trailhead	2430	3	-83.4666	35.69444	1994-1996
58	Roaring Fork at boundary gate	1840	3	-83.4834	35.71248	1994-1996
59	LeConte Creek near Bullhead Trail	2600	2	-83.4864	35.67414	1994-1996
60	LeConte Creek at log bridge	3520	2	-83.4707	35.66308	1994-1996
61	Unnamed tributary to LeConte Creek	3900	1	-83.4713	35.66095	1994-1996
62	Unnamed tributary to LeConte Creek	4060	1	-83.468	35.66079	1994-1996
63	LeConte Creek above Rainbow Falls	4550	2	-83.4598	35.66108	1994-1996
64	LeConte Creek below log bridge	2850	2	-83.4828	35.67048	1994-1996
65	Upper Big Branch (West Prong Little Pigeon)	2840	2	-83.4976	35.65535	1995-1995
66	West Prong Little Pigeon at Chimneys Picnic Area	2680	4	-83.4932	35.63712	1993-2009
67	Unnamed tributary at Chimneys Picnic Area	2840	2	-83.4873	35.63641	1994-1996
68	West Prong Little Pigeon above Chimneys Picnic Area	2830	4	-83.4865	35.63708	1993-1996
69	Bearpen Hollow (West Prong Little Pigeon)	3660	1	-83.4625	35.63667	1993-1996
70	Road Prong at Chimneys Trail split	3770	3	-83.47	35.62604	1993-1996
71	Road Prong above barrier cascade	3480	3	-83.4683	35.63256	1993-2009
72	Road Prong below barrier cascade	3360	3	-83.47	35.63403	1993-1996
73	Walker Camp Prong above Road Prong	3360	3	-83.4692	35.63474	1993-2009
74	Walker Camp Prong above Alum Cave Creek	3820	2	-83.4512	35.62943	1993-2009
75	Alum Cave Creek above Walker Camp Prong	3820	3	-83.4506	35.62962	1993-1996
76	Alum Cave Creek at fish site	3910	3	-83.4458	35.6311	1993-1996
77	Styx Branch above Rock Arch	4090	2	-83.4384	35.63807	1994-1996
78	Unnamed tributary to Styx Branch	4370	2	-83.4401	35.63619	1994-1996
79	Alum Cave Creek above Styx Branch	4280	2	-83.4375	35.63398	1993-1996
80	Unnamed tributary to Walker Camp at road	4690	2	-83.4107	35.6276	1993-1996
81	Unnamed tributary to Upper Walker Camp	4900	1	-83.4047	35.62905	1994-1996
82	Unnamed tributary to Kephart Prong at Icewater	5910	1	-83.3866	35.63082	1994-1996
83	Middle Prong Little Pigeon above Porters	1890	4	-83.3649	35.70386	1993-1996
84	Mid Prong Little Pigeon at Ramsay trailhead	2040	4	-83.3576	35.70301	1994-1996
85	Tributary at Ramsay Cascades Trailhead	2070	1	-83.3566	35.70239	1993-1993

Site ID	Site Description	Elev. (ft)	Stream Order	Longitude	Latitude	Survey period
86	Middle Prong Little Pigeon below Ramsay Prong	2600	4	-83.3341	35.70278	1994-1996
87	Middle Prong Little Pigeon above Ramsay Prong	2630	3	-83.3331	35.7017	1993-1996
88	Ramsay Prong above Middle Prong Little Pigeon	2630	3	-83.3332	35.70311	1994-1996
89	Ramsay Prong at second log bridge	3000	3	-83.3254	35.70681	1994-1996
90	Ramsay Prong above unnamed tributary (91)	3480	2	-83.3142	35.70927	1993-1996
91	Unnamed tributary to Ramsay Prong	3670	1	-83.3104	35.70966	1994-1996
92	Unnamed tributary to Ramsay Prong below falls	4280	1	-83.3011	35.70862	1994-1996
93	Ramsay Prong below falls	4380	2	-83.3021	35.70813	1993-1996
94	Ramsay Prong above falls	4480	2	-83.2995	35.7087	1993-1994
95	Upper Ramsay Prong	5000	2	-83.2898	35.70475	1993-1994
96	Eagle Rocks Creek above Buck Fork	3000	2	-83.3233	35.69537	1994-1995
97	Buck Fork above Eagle Rocks Creek	3000	3	-83.3239	35.6952	1995-1995
99	Lower Grassy Branch (Kephart Prong)	3590	1	-83.3606	35.62675	1994-1996
100	Now referred to as site 147	2460	4	-83.0728	35.66686	1995-1996
101	Right Raven Fork at Three Forks	4210	3	-83.2625	35.64516	1994-1995
102	Raven Fork below Three Forks pool	4210	2	-83.2618	35.64428	1994-1995
103	Otter Creek (Indian Camp Prong)	4300	1	-83.2571	35.73048	1993-2003
104	Copperhead Branch (Indian Camp Prong)	4160	1	-83.2643	35.72747	1993-2003
105	Unnamed tributary to Otter Creek	4100	1	-83.2689	35.72842	1993-1996
106	Upper Indian Camp Prong	3840	3	-83.2717	35.72758	1993-2003
107	Indian Camp below Albright Grove	3040	3	-83.2779	35.73753	1993-2003
108	Chasm Prong (Upper Bradley Fork)	3400	2	-83.3308	35.63418	1994-1995
109	Gulf Prong (Upper Bradley Fork)	3400	2	-83.3299	35.63509	1994-1995
110	Enloe Creek at Pecks Corner Shelter	5230	1	-83.3082	35.65087	1994-1996
111	Left Raven Fork at Tricorner Shelter	5920	1	-83.2569	35.69359	1994-1996
112	Buck Fork on AT near Tricorner Knob	6120	1	-83.2551	35.69738	1994-1996
113	Ramsay Prong on AT near Mt. Guyot	6500	1	-83.2612	35.70684	1994-1996
114	Cosby Creek at log bridge	2510	3	-83.2006	35.74824	1993-2009
115	Upper Cosby Creek	3840	1	-83.1835	35.74238	1994-2003
116	Rocky Branch at Cosby Shelter	4640	1	-83.1831	35.72617	1995-1996
117	Unnamed tributary to Big Creek	4200	1	-83.2112	35.72102	1994-1996
118	Upper Big Creek	3800	3	-83.2122	35.71541	1994-1996
119	Unnamed tributary to Big Creek	3700	3	-83.2049	35.71762	1994-1996
120	Big Creek above Gunter Fork area	3700	3	-83.1904	35.71573	1994-1996
121	Big Creek at Gunter Fork crossing	3180	3	-83.1767	35.70945	1993-1996
122	Lower Gunter Fork (Big Creek)	3380	3	-83.1769	35.70605	1994-1996
123	Lower Low Gap Branch (Big Creek)	3200	2	-83.1652	35.73076	1993-1996
124	Upper Low Gap Branch (Big Creek)	3800	1	-83.1768	35.73561	1993-1996
125	Ledge Creek (Straight Fork)	3550	2	-83.1944	35.62867	1994-1996
126	McGee Springs (Raven Fork)	5000	1	-83.2406	35.63952	1993-1996
127	Pretty Hollow Creek above Palmer Creek	2860	3	-83.1287	35.63977	1993-2003
128	Unnamed tributary to Pretty Hollow Creek	3440	1	-83.1333	35.65221	1994-1996
129	Pretty Hollow Creek at log bridge	3790	2	-83.1368	35.66328	1993-1996
130	Onion Bed Branch (Cataloochee Creek)	4150	2	-83.1398	35.6721	1993-1995
131	Unnamed tributary to Swallow Fork (Big Creek)	4280	1	-83.1428	35.69287	1993-1996
132	Middle Swallow Fork (Big Creek)	3700	2	-83.1518	35.69954	1993-1996

Site ID	Site Description	Elev. (ft)	Stream Order	Longitude	Latitude	Survey period
133	Lower Swallow Fork (Big Creek)	3280	3	-83.1605	35.70745	1993-1996
134	Big Creek below Swallow Fork	2970	4	-83.1642	35.71801	1993-1996
135	Big Creek at Brakeshoe Springs	2520	4	-83.1463	35.73579	1993-1996
136	Kilby Branch (Big Creek)	1880	4	-83.1274	35.74004	1994-1995
137	Upper Rock Creek (Cosby Creek)	2750	2	-83.2164	35.746	1993-2009
138	Inadu Creek (Cosby Creek)	3240	2	-83.2274	35.74234	1993-2009
139	Unnamed tributary at Laurel Gap Shelter	5600	1	-83.1915	35.66153	1994-1995
140	Falling Rock Creek (Cataloochee Creek)	3500	1	-83.1526	35.63425	1994-1996
141	Beech Creek above Falling Rock Creek	3500	3	-83.1526	35.63493	1994-1996
142	Beech Creek above Lost Bottom Creek	2900	3	-83.1451	35.63554	1994-2009
143	Lost Bottom Creek (Cataloochee Creek)	3100	2	-83.1469	35.63762	1994-2009
144	Palmer Creek above Pretty Hollow Creek	2860	3	-83.1304	35.63871	1993-2009
145	Caldwell Fork above Cataloochee Creek	2620	3	-83.0892	35.62851	1994-1996
146	Palmer Creek at Pretty Hollow Trailhead	2730	4	-83.1129	35.62631	1994-1996
147	Lower Cataloochee Creek	2460	4	-83.0728	35.66686	1993-2009
148	Lower Little Cataloochee Creek	2475	4	-83.0729	35.66891	1993-2009
149	Mid Cataloochee Creek at bridge	2550	4	-83.0755	35.64646	1993-2009
150	Cataloochee Creek below Caldwell Fork	2620	4	-83.0864	35.63071	1994-2003
151	Wilson Branch near Abrams Falls	1480	2	-83.879	35.60976	1993-1996
152	Abrams Creek below Abrams Falls	1450	4	-83.8801	35.60851	1993-1996
153	Abrams Creek at Hanna Mountain Trail crossing	1260	4	-83.899	35.60529	1994-1996
154	Rabbit Creek at Rabbit Creek Trail crossing	1720	1	-83.9126	35.59751	1994-1994
155	Scott Gap Branch at Hanna Mountain Trail	1450	3	-83.906	35.59258	1994-1994
156	Abrams Creek at ranger station	1110	4	-83.9351	35.60921	1994-2003
157	Rabbit Creek Spring	2620	1	-83.8883	35.54373	1993-1996
158	Panther Creek at Parson Branch Road	2520	2	-83.8968	35.53751	1993-1996
159	Upper Parsons Branch Road	2540	1	-83.9048	35.53581	1993-1996
160	Middle Parsons Branch	2000	1	-83.9217	35.52662	1993-1996
161	Bible Creek above Parsons Branch	1600	3	-83.9253	35.50624	1993-1996
162	Parsons Branch below Bible Creek	1580	3	-83.9264	35.50515	1993-1996
163	Upper Beard Cane Creek	1650	1	-83.8767	35.6307	1995-1996
164	Wilson Branch at Cooper Road	1730	3	-83.8693	35.6229	1995-1996
165	Tributary to Wilson Branch	1870	1	-83.8641	35.62086	1995-1996
166	Stony Branch at Cooper Road	1950	1	-83.8544	35.61878	1995-1996
167	Arbutus Creek at Cooper Road	1990	1	-83.8477	35.6477	1995-1996
168	Panther Creek above lowest tributary	1990	3	-83.9774	35.55591	1994-1996
169	Lowest tributary to Panther Creek	900	1	-83.9851	35.55416	1995-1996
170	Lower Panther Creek	860	3	-83.9883	35.55544	1994-1996
171	Chilhowee Lake at Abrams Creek	860	4	-83.9986	35.55577	1993-1996
172	Lower Tabcat Creek	890	3	-83.9904	35.52436	1993-1996
173	Mill Creek above Abrams Creek	1705	3	-83.8534	35.59084	1993-2009
174	Abrams Creek below Cades Cove	1705	4	-83.8533	35.59177	1993-2009
175	Stony Branch (Abrams Creek)	1560	1	-83.8718	35.60665	1993-1996
176	Abrams Creek above Stony Branch	1560	4	-83.8719	35.60606	1993-1996
177	Forge Creek at Parsons Branch Road	2180	3	-83.8466	35.56232	1993-1996
178	Panther Creek below Gregory Bald	3900	1	-83.8737	35.52803	1993-1995

Site ID	Site Description	Elev. (ft)	Stream Order	Longitude	Latitude	Survey period
179	Gunna Creek above Mill Creek (Eagle)	2400	3	-83.752	35.52677	1994-1995
180	Mill Creek above Eagle Creek	2400	3	-83.7549	35.52597	1994-1995
181	Eagle Creek at campsite 96	1990	4	-83.7605	35.50574	1994-1995
182	Spring at The Dungeon (20 Mile Creek)	3660	1	-83.8144	35.50198	1994-1994
183	Spring at Russell Field Shelter	4270	1	-83.7678	35.56283	1994-2003
184	Left Fork Anthony Creek at camp 10	2830	1	-83.7585	35.58013	1994-2003
185	Anthony Creek below fork (left and right)	2280	3	-83.7604	35.59225	1993-1996
186	Anthony Creek above picnic area	1965	3	-83.7692	35.60406	1993-2003
187	Abrams Creek above picnic area	1960	1	-83.7695	35.60534	1993-1996
188	Panther Creek above Lynn Camp Prong	3240	1	-83.6287	35.61211	1993-1996
189	Lynn Camp Prong above Middle Prong Little River	2590	3	-83.6371	35.60789	1993-1996
190	Thunderhead Prong at trail crossing	2160	2	-83.6721	35.60834	1994-2003
191	Sams Creek (Middle Prong Little River)	3240	2	-83.6575	35.5819	1993-2003
192	Starkey Creek (Middle Prong Little River)	3200	2	-83.6588	35.5819	1993-2003
193	Middle Prong Little River at old trailhead	1960	3	-83.6683	35.61572	1993-2003
194	Middle Prong Little River above Tremont	1700	4	-83.6783	35.62079	1993-2003
195	Spring at Spence Field Shelter	4500	1	-83.7337	35.56237	1994-2003
196	Gunna Creek above Devils Race Branch	3780	2	-83.7337	35.5492	1994-1995
197	Gunna Creek at old campsite	3040	2	-83.7409	35.54221	1994-1995
198	Gunna Creek at 2500 ft	2500	3	-83.7481	35.531	1994-1995
199	Unnamed tributary at Campsite 82 (Hazel)	2800	3	-83.6425	35.51706	1993-1996
200	Anthony Creek above Campsite 9	3720	2	-83.7409	35.57794	1993-2003
201	Anthony Creek below Spence Field	4800	1	-83.731	35.56493	1994-2003
202	Unnamed tributary on Jenkins Ridge Trail	4800	1	-83.71	35.5573	1994-1994
203	Little River (below Fish Camp and Campsite 30)	3100	3	-83.5198	35.60542	1993-1993
204	Little River at Campsite 30	3500	2	-83.5144	35.59476	1993-1993
205	Grouse Creek at Campsite 30	3500	2	-83.5153	35.59443	1993-1993
207	Jakes Creek at 3640	3640	1	-83.6031	35.62063	1994-1996
208	Upper Panther Creek (Middle Prong Little River)	2590	3	-83.6163	35.61579	1993-1996
209	Lost Creek (Little River)	2925	1	-83.5372	35.62077	1993-2003
210	Little River above Fish Camp Prong	2740	4	-83.5386	35.61954	1993-2003
211	Fish Camp Prong below Ashe Camp Prong	2740	3	-83.5394	35.6189	1993-1996
212	Fish Camp Prong above Little River	3300	3	-83.5681	35.59979	1993-1996
213	Goshen Prong above Fish Camp Prong	3360	3	-83.5678	35.59849	1993-2003
214	Silers Creek (Little River)	3400	2	-83.5677	35.59472	1993-2003
215	Ashe Camp Prong (Little River)	3380	2	-83.5701	35.59948	1993-2003
216	Buckeye Gap Prong at Campsite 25	3600	2	-83.5793	35.58823	1994-1994
218	Spring at Silers Bald Shelter	5440	1	-83.5688	35.56488	1994-2003
219	Double Springs Gap Shelter (NC side)	5510	1	-83.5427	35.56445	1994-2003
220	Double Springs Gap Shelter (TN side)	5500	1	-83.5428	35.56603	1994-2003
221	Hazel Creek above cascades	4000	2	-83.5822	35.54804	1993-2009
222	Hazel Creek at 3400 ft.	3400	1	-83.6029	35.53477	1994-1996
223	Proctor Creek (Hazel Creek)	3060	2	-83.6203	35.53126	1993-1996
224	Hazel Creek below Proctor Creek	3000	3	-83.6222	35.52797	2004-2009
225	Upper Forney Creek	4800	1	-83.5074	35.54496	1993-1996
226	Forney Creek below Keeyuga Creek	4370	2	-83.5128	35.53991	1993-1996

Site ID	Site Description	Elev. (ft)	Stream Order	Longitude	Latitude	Survey period
227	Steeltrap Creek (Forney Creek)	3930	2	-83.515	35.54069	1993-1996
228	Forney Creek above Little Steeltrap	3310	3	-83.5274	35.53246	1993-1996
229	Huggins Creek at Campsite 69	2760	3	-83.5413	35.52347	1993-1996
230	Forney Creek at Campsite 69	2760	3	-83.5418	35.52277	1993-1996
231	Forney Creek at Jonas Creek Trail	2460	4	-83.5544	35.51471	1993-1996
232	Unnamed tributary to West Prong Little Pigeon River	4210	1	-83.4313	35.61814	1993-1996
233	Walker Camp Prong above Alum Cave	4240	2	-83.4274	35.61821	1993-2009
234	Upper Road Prong	5000	1	-83.4508	35.60981	1993-2009
235	Road Prong at only stream crossing	4000	3	-83.47	35.62122	1993-1996
236	Unnamed tributary to Walker Camp Prong	4470	1	-83.4167	35.62377	1993-1996
237	Walker Camp Prong at last bridge	4510	2	-83.417	35.62413	1993-2009
242	Spring at Mt. Collins Shelter (Road Prong)	5830	1	-83.4739	35.59416	1994-1996
243	Clingmans Creek (Noland Creek)	5580	1	-83.4839	35.56001	1993-1996
244	NE stream at Noland Divide Watershed	5150	1	-83.4803	35.56465	1993-1996
245	Sassafras Branch (Noland Creek)	3550	1	-83.4591	35.53116	1993-1996
246	Noland Creek at Campsite 61	3530	3	-83.4661	35.52948	1993-1996
247	Noland Creek at first crossing	3185	3	-83.4681	35.51393	1993-1996
248	Noland Creek at third crossing	2980	3	-83.4808	35.50911	1993-1996
249	Unnamed tributary just below site 248	2950	1	-83.4825	35.50874	1993-1996
250	Beech Flats at 3500 ft.	3500	3	-83.3966	35.59652	1993-1996
251	Beech Flats above US 441 loop	4010	2	-83.4157	35.60223	1993-2009
252	Beech Flats below roadcut	4760	1	-83.435	35.60691	1993-2009
253	Beech Flats above roadcut	4840	1	-83.4369	35.60746	1993-2009
254	Upper Deep Creek	4120	1	-83.4281	35.59689	1993-1996
255	Deep Creek at 3820	3820	1	-83.428	35.59016	1993-1996
256	Deep Creek at 3215	3215	3	-83.4255	35.56846	1993-1996
257	Deep Creek at Campsite 53	3000	3	-83.4186	35.56124	1993-1996
258	Deep Creek at Campsite 54	2640	3	-83.4121	35.54509	1993-1996
259	Deep Creek at Campsite 58	2400	1	-83.4209	35.52038	1994-1996
260	Kephart Prong above Beech Flats	2800	3	-83.3624	35.58923	1993-1996
261	Kephart Prong at 3020 ft	3020	3	-83.3642	35.59545	1993-1996
262	Coon Branch (Kephart Prong)	3360	3	-83.3658	35.60512	1993-1996
263	Kephart Prong at Kephart Shelter	3590	2	-83.3698	35.60986	1993-1996
264	Lower Lower Grassy Branch (Kephart)	4210	1	-83.3636	35.62008	1993-1996
265	Couches Creek (Oconaluftee River)	2100	5	-83.3034	35.53627	1993-1996
266	Oconaluftee River at Visitors Center	2020	5	-83.3062	35.51591	1993-2003
267	Raven Fork near park housing	2035	5	-83.2991	35.51377	1993-1996
268	Oconaluftee River below Smokemont	2170	5	-83.3096	35.55325	1994-2009
269	Oconaluftee River above Collins Creek	2220	4	-83.3391	35.57304	1993-1996
270	Beech Flats at Kephart footbridge	2800	3	-83.3585	35.58589	2004-2009
271	Chasteen Creek at Campsite 50	2370	3	-83.3124	35.57738	1993-1996
272	Unnamed tributary at Campsite 48	3500	2	-83.2895	35.59958	1993-1996
273	Unnamed tributary to Chasteen Creek	3830	1	-83.2838	35.60006	1993-1996
274	Unnamed tributary to Chasteen Creek	3960	1	-83.2835	35.60238	1994-1996
275	Unnamed tributary to Chasteen Creek	4100	1	-83.2858	35.60412	1994-1996
276	Enloe Creek at log bridge	3970	3	-83.2702	35.61376	1993-1996

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277	Raven Fork at Campsite 47	3620	4	-83.2549	35.6101	1993-1996
278	Upper Taywa Creek	4000	2	-83.321	35.6059	1994-1996
279	Lower Taywa Creek	3380	1	-83.3099	35.61822	1994-1996
280	Bradley Fork at end of road	2930	3	-83.3327	35.60609	1994-1996
281	Bradley Fork at 2750	2750	3	-83.3257	35.59615	1994-1996
282	Bradley Fork above Chasteen Creek	2370	4	-83.3122	35.57529	1993-1996
283	Bradley Fork above Smokemont Camp	2260	4	-83.3102	35.56326	1993-1996
284	Bradley Fork at Campsite 49	3040	3	-83.3282	35.61538	1994-1996
285	Hurricane Creek above Rough Fork	3030	1	-83.1315	35.59985	1993-1996
286	Rough Fork above Hurricane Creek	3030	3	-83.1312	35.60247	1994-1996
287	Rough Fork below Messer Fork	2950	3	-83.1287	35.61122	1993-1996
288	Hyatt Creek (Straight Fork)	3640	1	-83.2315	35.61724	1993-1996
289	Straight Fork at concrete slab crossing	3070	4	-83.212	35.62283	1993-1996
290	Bear Branch at Campsite 42 (Cataloochee)	5500	1	-83.18	35.6067	1994-2003
291	Bunches Creek above Balsam Mountain Road	5320	1	-83.1744	35.57405	1994-2003
292	Straight Fork at Enloe Creek Trail	2910	4	-83.2234	35.60773	1994-1996
293	Rough Fork at Caldwell House	2730	3	-83.1143	35.624	1993-2009
294	Caldwell Fork near Campsite 41	3240	3	-83.1221	35.586	1993-1996
295	Caldwell Fork at Rabbit Ridge Trail	3000	3	-83.104	35.59879	1993-1996
296	Snake Branch (Cataloochee Creek)	3020	1	-83.1004	35.60283	1994-1996
297	Caldwell Fork below Sag Branch	2800	3	-83.0958	35.61519	1994-1996
298	Parsons Branch at boundary	1550	3	-83.934	35.49934	1993-1996
299	Twentymile Creek at ranger station	1270	3	-83.8778	35.46683	1993-1996
300	Ekaneetlee Creek above Eagle Creek	1890	4	-83.7644	35.49773	1994-1996
301	Eagle Creek at Campsite 89	1890	4	-83.764	35.49702	1994-1996
302	Eagle Creek at Campsite 90	1760	4	-83.7769	35.4841	1994-1996
303	Lost Cove Creek (Eagle Creek)	2920	4	-83.8072	35.48977	1994-1994
304	Proctor Branch above 20 mile Creek	2500	2	-83.8451	35.4815	1994-1996
305	Twentymile Creek at upper bridge	2300	3	-83.8321	35.48735	1994-1996
306	Twentymile Creek above Campsite 93	2200	3	-83.8517	35.47338	1994-1996
307	Dalton Branch above 20 mile Creek	1470	2	-83.8708	35.47216	1994-1996
308	Pinnacle Creek above Eagle Creek	1850	2	-83.7667	35.48928	1994-1995
309	Unnamed tributary to Eagle Creek	1800	1	-83.7952	35.4695	1994-1995
310	Bone Valley Creek (Hazel Creek)	2280	3	-83.6803	35.49994	1993-2009
311	Hazel Creek below Haw Gap Creek	2190	4	-83.6886	35.49375	1993-2009
312	Hazel Creek at Campsite 85	1770	4	-83.6963	35.48371	1994-1996
313	Forney Creek at Lake Shore Trail	1770	4	-83.5639	35.44182	1996-1996
314	Noland Creek at Campsite 66	1770	4	-83.5245	35.44754	1995-1995
315	Forney Creek at Campsite 71	2160	1	-83.5637	35.48448	1993-1996
316	Gray Wolf Creek at Lakeshore Trail	2200	2	-83.5561	35.47575	1993-1995
317	Unnamed tributary to Goldmine Branch, Noland	2520	1	-83.5402	35.46901	1993-1995
318	Unnamed tributary to Goldmine Branch, Noland	2240	2	-83.5333	35.4681	1993-1995
319	Slab Cove Branch (Noland Creek)	2540	1	-83.5054	35.4968	1994-1996
320	Noland Creek below Campsite 64	2510	4	-83.5039	35.49683	1995-1996
321	Bearpen Branch at Campsite 65	1990	4	-83.5188	35.46945	1994-1996
322	Noland Creek below Road-to-Nowhere	1790	4	-83.5267	35.45823	1994-1996
323	Deep Creek at first large bridge	2000	3	-83.4252	35.48874	1993-1996

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324	Indian Creek at trail bridge	1880	2	-83.4291	35.47251	1994-1996
325	Deep Creek above campgrounds	1820	3	-83.434	35.46413	1993-1996
326	Deep Creek at boundary	1780	3	-83.4381	35.45837	1993-1996
327	Oconaluftee River at boundary	1990	6	-83.2999	35.49968	1993-1996
328	Grass Branch (Straight Fork)	3890	1	-83.224	35.62552	1994-1996
329	Unnamed tributary to Anthony Creek	3600	1	-83.7357	35.58011	1994-1996
330	War Branch (Little River)	3000	1	-83.5487	35.60808	1994-1996
331	Shields Branch (Little River)	2700	1	-83.5969	35.6433	1994-1996
332	Trib to Raven Fork above Campsite 47	4100	1	-83.2525	35.60912	1994-1996
333	Boulevard Prong (Middle Prong Little Pigeon)	2760	2	-83.4228	35.67421	1995-1996
334	Trillium Branch (Middle Prong Little Pigeon)	3750	1	-83.3981	35.66678	1995-1995
335	Abrams Creek at Campsite 17	1200	4	-83.9069	35.61119	1995-1996
336	Flat Creek above falls (Bunches Creek)	4680	2	-83.1732	35.54972	1995-2003
337	Bunches Creek at Flat Creek Trail	4740	2	-83.1678	35.55456	1995-2003
338	Left Raven Fork above Three Forks	4210	2	-83.2645	35.64436	1994-1995
339	Little Cataloochee (use 148 instead)	2475	4	-83.0729	35.66891	1996-1996
340	Kiver Branch (Little River)	2520	1	-83.6061	35.64779	1995-1996
341	Kreider Branch (Abrams Creek)	1350	2	-83.8909	35.61119	1995-1996
342	Oak Flats (Abrams Creek)	1320	2	-83.893	35.60912	1995-1996
343	Rye Patch Branch (Twentymile Creek)	2950	1	-83.8406	35.50173	1995-1995
344	Twentymile Creek at Campsite 92	2650	3	-83.8343	35.49931	1995-1995
345	Middle Prong Little Pigeon below Buck Fork	2850	3	-83.3255	35.69596	1995
346	Bulldie Creek (Raven Fork)	4180	2	-83.2691	35.63208	1995
347	Dudley Creek at the stable on US 321	1300	3	-83.4534	35.72997	1995
348	Middle Raven Fork above Three Forks	4210	2	-83.2626	35.64434	1995
349	Tributary to Raven Fork near Campsite 47 (Ramp)	3800	1	-83.2506	35.6143	1995
350	Tributary to Bunches on Flat Creek Trail	4750	1	-83.1653	35.55922	1995-1996
351	Tributary to Panther Creek on course	910	1	-83.9916	35.55525	1996-1996
352	Shop Creek above impoundment	900	3	-83.9908	35.53108	1995-1996
353	Mannis Branch (Little River)	2560	1	-83.6212	35.6471	1995-1996
354	Henderson Prong (Little River)	2860	1	-83.638	35.64123	1995-1996
355	Bunch Prong (Meigs Creek, Little River)	2270	1	-83.6495	35.64883	1995-1996
356	Unnamed tributary on Breakneck Ridge	5500	1	-83.2542	35.63674	1995
357	Tributary to Straight Fork	3300	1	-83.1791	35.62845	1995-1996
358	Bee Gum Branch (Forney Creek)	3610	1	-83.5419	35.49776	1995-1995
359	Springhouse Branch (Noland Creek)	3300	2	-83.5101	35.51243	1995-1995
360	Upper Walker Camp	4710	1	-83.4111	35.62759	1993-1995
361	Clingmans Dome (Forney Creek)	6240	1	-83.4992	35.55974	1996-1996
362	Kenati Fork (Oconaluftee River)	2840	2	-83.3633	35.58702	1995-1996
363	Straight Fork at boundary	2560	4	-83.2422	35.57873	1995-1996
364	Big Creek at boundary	1560	4	-83.1129	35.7614	1995-1996
366	Kingfisher Creek (89)	1590	2	-83.9239	35.61844	1993-1996
367	149C	3520	2	-83.2903	35.60048	1993-1993
368	Gabes Creek (Cosby Creek)	3300	1	-83.2456	35.7462	1995
369	Right Prong of Ledge Creek near Campsite 42	5080	1	-83.1804	35.61102	1995-1996
377	Gillalard Creek	2660	1	-83.1804	35.76657	1995-1996

Site ID	Site Description	Elev. (ft)	Stream Order	Longitude	Latitude	Survey period
392	Mill Creek above confluence with Springhouse Branch at 2830 ft.	2830	3	-83.5013	35.50622	1995-1995
393	Mill Creek at Campsite 64	2544	3	-83.5525	35.4981	1996-1996
399	Unnamed tributary to Cold Spring Branch	4180	1	-83.6729	35.49344	1996-1996
400	Cold Spring Branch at first trail crossing	3600	1	-83.6351	35.49517	1996-1996
401	Cold Spring Branch at second trail crossing	2870	2	-83.6525	35.4981	1996-1996
402	Cold Spring Branch	2500	2	-83.6594	35.50207	1996-1996
472	Sams Creek above Thunderhead Prong	2160	3	-83.667	35.608	1996-2003
473	West Prong Little Pigeon River across from Bearpen Prong	3660	3	-83.463	35.6362	1996-2003
474	Little River below Husky Branch at resting bench	2440	5	-83.557	35.647	1996-2003
475	Fish Camp Prong at angled barrier below War Branch	2960	4	-83.548	35.6083	1996-2003
479	Hazel Creek at Campsite 86	1750	5	-83.719	35.4723	1996-2009
480	Haw Gap Creek at bridge near Campsite 84	2200	3	-83.689	35.4947	1996-2009
481	Little Fork above Sugar Fork Trail	2660	1	-83.708	35.5026	1996-2009
482	Sugar Fork above Little Fork	2680	2	-83.709	35.5024	1996-2009
483	Sugar Fork above Haw Gap Creek	2270	3	-83.695	35.4995	1996-2009
484	Hazel Creek at Cold Spring Gap Trail	2830	4	-83.659	35.5033	1996-2009
485	Walker Creek above Hazel Creek Trail	3080	3	-83.631	35.5225	1996-2009
486	Unnamed tributary to Hazel on Cascades Trail	4240	1	-83.5808	35.54917	1996-1996
487	Peachtree Creek above Road to Nowhere	2760	2	-83.4825	35.455	1996-1996
488	Mill Creek at Pumphouse on Forge Creek Road	2070	3	-83.834	35.5835	1996-2009
489	Abrams Creek 300 m below trailhead bridge	2200	4	-83.854	35.5914	1996-2009
490	Little River at bench below Husky Branch	2440	4	-83.553	35.64824	1996-1996
492	Camel Hump Creek off Low Gap Trail		2	-83.199	35.7446	1996-2009
493	Palmer Creek at Davidson Branch Trail	3000	3	-83.119	35.6346	1996-2009
494	Horse Cove Creek		2	-83.5087	35.4765	1996-1996

Appendix 2. Collocated Stream Survey Sites with Water Quality, Fish, and Macroinvertebrate Data.

No.	Location	Macroinvertebrate site	Macroinvertebrate sample years	Fish Site	Fish sample years	Stream survey site	Chemistry sample years
1	Indian Camp Creek at Old Settlers	ICIC01I&M	1996	ICC-2	1992-1995, 1997-2004, 2006-2009	1	1993-2003
2	Lower Rock Creek	CBRC01I&M	1993-1997	ROC-2	1993-2005	4	1993-
3	Lower Cannon Creek	MPCA01I&M	1994, 1996	CAN-1	1995-2002, 2009	47	1994-2003
4	Road Prong above barrier cascade	WPRP01I&M	1993-2003	RPR-5	1993-2009	71	1993-
5	Alum Cave Creek above Walker Camp Prong	WPAL01I&M	1993-1994	ALC-1	1993-1995	75	1993-1996
6	Indian Camp below Albright Grove	ICIC02I&M	1996	ICC-3N	1994-1995, 1997-2009	107	1993-2003
7	Upper Rock Creek (Cosby Creek)	CBRC02I&M	1992, 1994-2003	ROC-7	1991-2009	137	1993-
8	Lost Bottom Creek (Cataloochee Creek)	CTLB01I&M	1992-2003	LOB-0	1994-2005	143	1994-
9	Little Cataloochee Creek, above Cataloochee Creek	CTLC01I&M	1990	LCT-1M	1998	148	1993-
10	Abrams Creek at Ranger Station (lower)	ABAB01I&M	1994-2003	ABC-1	1993-2000	156	1994-2003
11	Thunderhead Prong above Sams Creek	MLTH02I&M	1996	THD-C1	2000-2003, 2005	190	1994-2003
12	Sams Creek (Middle Prong Little River)	MLSA02I&M	1993-1995, 1998-2000, 2002-2003	SAM-6	1990, 1992-1999, 2003-2008	191	1993-2003
13	Starkey Creek above Sams Creek	MLST01I&M	1993-1996, 1998-1999, 2001-2003	STK-1	1990, 1992-1999, 2003-2008	192	1993-2003
14	Silers Creek above Fish Camp Prong	ELSI01I&M	1993-2003	SIL-1	1992-2005	214	1993-2003
15	Ash Camp Prong	ELAS01I&M	1993-1994, 1996	ACB-1	1993, 1998, 2001-2002	215	1993-2003
16	Taywa Creek above Bradley Fork	BRTA01I&M	1993-2003	TAY-2	1992	279	1994-1996
17	Straight Fork above low water ford crossing	SRSF02I&M	1994	STR-2	1990-1993, 1998-2000, 2005-2006, 2009	289	1993-1996
18	Flat Creek above falls (Bunches Creek)	BNFL01I&M	1994-2003	FLT-1	1992-2008	336	1995-2003

No.	Location	Macroinvertebrate site	Macroinvertebrate sample years	Fish Site	Fish sample years	Stream survey site	Chemistry sample years
19	Bunches Creek at Flat Creek Trail	BNBU01I&M	1992, 1994-2003	BUN-1	1990-2009	337	1995-2003
20	Bunches Creek, 1000 m upstream of site BNBU01	BNBU02I&M	1994-2001	BUN-2	1990-2009	337	1995-2003
21	Hazel Creek at Cold Spring Gap Trail	HZZH02I&M	1995-2003	HAZ-1	1996-1999, 2002	484	1996-
22	Abrams Creek 300m below trailhead bridge (upper)	ABAB02I&M	1994-2003	ABC-2	1993-2000, 2007	489	1996-
23	Palmer Creek at Davidson Branch Trail	CTPC02I&M	1990, 1994-2003	CAT-4	1990-2003, 2008	146,493	1994-1996, 1996-
24	Dunn Creek at boundary			DUN-0	1993	2	1994-1995
25	Little River (lower)			LRV-0	1996-1998	13	1993-
26	Little River (middle)			LRV-1	1991-1994, 1996-1999, 2001-2003, 2006-2007	20	1993-2003
27	Little River (upper)			LRV-2	1991-1994, 1996-1999, 2001-2003	34	1993-2003
28	Laurel Branch at Laurel Falls			LBR-2	1992	36	1995-1996
29	Alum Cave Creek at fish site			ALC-3	1993-1994	76	1993-1996
30	Cosby Creek			COS-2	1995-2009	114	1993-
31	Pretty Hollow Creek at log bridge			PTH-2	1991-1993	129	1993-1996
32	Beech Creek above Lost Bottom Creek			BEC-1	1991-2005	142	1994-
33	Cataloochee Creek (lower)			CAT-1	1990-2003, 2008	147	1993-
34	Cataloochee (middle)			CAT-2	1990-2003, 2008	149	1993-
35	Cataloochee Creek (upper)			CAT-3	1990-2003, 2009	150	1994-2003
36	Bible Creek above Parsons Branch			BIB-1	1997-1998	161	1993-1996
37	Mill Creek above Abrams Creek (Lower)			MIL-1	1993-1999, 2002, 2009	173	1993-
38	Abrams Creek below Cades Cove			ABC-3	1993-2000, 2002, 2007	174	1993-
39	Anthony Creek above Picnic Area			ANC-1	1993-2002	186	1993-2003

No.	Location	Macroinvertebrate site	Macroinvertebrate sample years	Fish Site	Fish sample years	Stream survey site	Chemistry sample years
40	Hazel Creek (upper)			HAZ-3	1996-2006, 2008-2009	221	1993-
41	Deep Creek at 3820			DPC-1	1997-2000	255	1993-1996
42	Parsons Branch at boundary			PAR-1	1997-1998	298	1993-1996
43	Twentymile Creek at Ranger Station			TWC-1	2002	299	1993-1996
44	Kenati Fork (Oconaluftee River)			KAN-1	1995-2009	362	1995-1996
45	Sams Creek (lower)			SAM-1	1990, 1995-2000, 2003-2009	472	1996-2003
46	Walker Creek			WAL-1N	1998-1999, 2004-2006, 2008-2009	485	1996-
47	Mill Creek at pump house on Forge Creek Road (upper)			MIL-2	1993-2002	488	1996-
48	Hesse Creek at Rich Mountain Road	HSBS02I&M	1997			8	1995-1996
49	Lower Beard Cane Creek	HSBC01I&M	1997			11	1995-1996
50	LeConte Creek at Uplands	LCLC01I&M	1995-2003			28	1994-1996
51	West Prong Little Pigeon at boundary	WPLP01I&M	1995-1996			29	1993-1996
52	Shutts Prong	MPSP01I&M	1994-1995, 2003			45	1993-2003
53	Raven Fork below Three Forks pool	RVRV03I&M	1995			102	1994-1995
54	Beech Creek above Falling Rock Creek	CTBE01I&M	1993-2003			141	1994-1996
55	Panther Creek above lowest tributary	PTPC01I&M	1994			168	1994-1996
56	Hazel Creek, above Proctor Creek	HZZH03I&M	1995-2001, 2003			224	2004-2006
57	Upper Forney Creek	FOUN02I&M	1994			225	1993-1996
58	Forney Creek below Keeyuga Creek	FOFO03I&M	1994			226	1993-1996
59	Forney Creek above Little Steeltrap	FOFO04I&M	1994			228	1993-1996
60	Beech Flats above US 441 loop	OWBF04I&M	1998			251	1993-
61	Kephart Prong above Beech Flats	OWKP01I&M	1998			260	1993-1996
62	Oconaluftee River above Collins Creek	OWOC02I&M	1998			269	1993-1996
63	Chasteen Creek at Campsite 50	BRCH01I&M	1998			271	1993-1996

No.	Location	Macroinvertebrate site	Macroinvertebrate sample years	Fish Site	Fish sample years	Stream survey site	Chemistry sample years
64	Indian Creek at trail bridge	DPIN01I&M	1997			324	1994-1996
65	Kingfisher Creek (89)	ABKF01I&M	1997			366	1993-1996
66	Hazel Creek, 800 m downstream of site HZHZ00	HZHZ01I&M	1995-2003			479	1996-
67	Camel Hump Creek above Cosby creek	CBCM01I&M	1996			492	1996-
68	Lost Bottom Creek, upstream of the confluence with an unnamed stream	CTLB02I&M	1992-1993, 2003	LOB-24	1990-1996		
69	Lost Bottom Creek, 1200 m upstream of site CTLB02	CTLB03I&M	1993-2002	LOB-34	1990-1997		
70	Lost Bottom tributary to an unnamed stream, above Lost Bottom Creek	CTTA02I&M	1994-1995	LBTRA-1	1990-1996		
71	Dunn Creek, second order	DNDN01I&M	1996	DUN-4	1993		
72	Bear Creek above Forney Creek	FOBC01I&M	1994	BRC-18	2003, 2005-2007		
73	Greenbrier Creek	GRGR01I&M	1996	GBC-1	1995		
74	Defeat Branch above Roaring Creek	HZDF01I&M	1995-1997, 2001-2002	DEF-1			
75	Beech Flats above Kephart footbridge	OWBF01I&M	1998	BEF-0	2007		

Appendix 3. Weather Stations Located in and near Great Smoky Mountains National Park.

Weather station name	Latitude	Longitude	Elevation (m)	State	Source
Bryson city	35.45	83.4333	591.3	NC	NOAA, TVA
Cades Cove	35.6042	83.7831	564	TN	NPS, TVA
Cataloochee	35.6333	83.1	807.7	NC	NOAA
Cherokee	35.6162	83.2145	977	NC	TVA
Clingmans Dome	35.5619	83.4981	2021	NC	NPS
Cosby	35.75	83.25	487.7	TN	TVA
Cove Mountain	35.6967	83.6086	1243	TN	NPS
Elkmont	35.6645	83.5903	640	TN	NADP
Fontana Dam	35.4816	83.8063	520	NC	TVA
Gatlinburg	35.6833	83.5333	443.2	TN	NOAA
Look Rock	35.6331	83.9422	793	TN	NPS
Mt. LeConte	35.65	83.4333	1979.1	TN	NOAA
Newfound Gap	35.6124	83.43	1524	TN	NOAA, TVA
Oconaluftee	35.5333	83.3167	621.8	NC	NOAA
Sams Gap	35.5716	82.3342			TVA
Sugarlands VC	35.6796	83.5313	487.68	TN	Morristown
Tapoco	35.45	83.9333	338.3	NC	NOAA
Walters Dam	35.4215	83.0231			TVA
Waterville	35.7667	83.1	438.9	NC	NOAA
Waynesville	35.4833	82.9833	829.1	NC	TVA

Appendix 4. PHREEQC Codes to Compute Aluminum Species Composition for Stream Chemistry Data.

SOLUTION_SPECIES

```
Fulvate-2 + H+ = HFulvate- #equilibrium constant from WHAM, Tipping (1994)
log_k -3.26
H+ + Humate-2 = HHumate- #equilibrium constant from WHAM, Tipping (1994)
log_k -4.02
Al+3 + Fulvate-2 = AlFulvate+ #equilibrium constant from Cloutler-hurteau et al. (2007) Comparing WHAM 6 and
MINEQL+ 4.5 for the chemical speciation of Cu2+ in the Rhizosphere of Forest Soils
log_k 4.6
Al+3 + Humate-2 = AlHumate+ #equilibrium constant from Cloutler-hurteau et al. (2007) Comparing WHAM 6
and MINEQL+ 4.5 for the chemical speciation of Cu2+ in the Rhizosphere of Forest Soils
log_k 6.62
13Al+3 + 28H2O = Al13O4(OH)24+7 + 32H+ #equilibrium constant from llnl database of PHREEQC
log_k -98.73
2Al+3 + 2H2O = Al2(OH)2+4 + 2H+ #equilibrium constant from llnl database of PHREEQC
log_k -7.6902
3Al+3 + 4H2O = Al3(OH)4+5 + 4H+ #equilibrium constant from llnl database of PHREEQC
log_k -13.8803
Al+3 + 2Fulvate-2 = AlFulvate2- #equilibrium constant from Cloutler-hurteau et al. (2007) Comparing WHAM 6
and MINEQL+ 4.5 for the chemical speciation of Cu2+ in the Rhizosphere of Forest Soils
log_k 3.5
SOLUTION_MASTER_SPECIES #Molecular weight from WHAM, Tipping (1994)
Fulvate Fulvate-2 0 650 650
Humate Humate-2 0 2000 2000
```

SOLUTION_SPREAD

```
#Assuming DOC = 0.75ppm (range 0.5 to 1.0 ppm from measurement for baseflow)
#Assuming 40% of DOC is fulvic acid and 10% of DOC is humic acid. This percentage distribution cited from
Thurman, E.M. (1985). Organic geochemistry of natural waters. PP105
pH Alkalinity Cl N(5) S(6) Na N(-3) K Mg Ca Al
Cu Fe Mn Si Zn Fulvate Humate
ueq/kgw uMol/kgw uMol/kgw uMol/kgw uMol/kgw uMol/kgw uMol/kgw
uMol/kgw uMol/kgw uMol/kgw mg/kgw mg/kgw
uMol/kgw uMol/kgw uMol/kgw
6.53 70.40 14.20 3.55 8.64 43.63 0.00 11.77 10.96 21.08 0.401548148
0 0.5012 0 122.3546071 0 0.3 0.075
..... # median values of each site were input here.
```

SELECTED_OUTPUT

```
-file F:\mcai\research\My project\Fish and biota\Model\PHREEQC\AlSpecies.out
-molalities Al(OH)2+ Al(OH)3 Al(OH)4- Al(SO4)2-
Al+3 AlFulvate+ AlHSO4+2 AlHumate+
AlOH+2 AlSO4+ HFulvate- HHumate-
Humate-2 Al13O4(OH)24+7 Al2(OH)2+4 Al3(OH)4+5
AlFulvate2- Fulvate-2
```


Appendix 5. Forest/Vegetation Cover, Soil, and Geology (Rock) Types in GRSM.

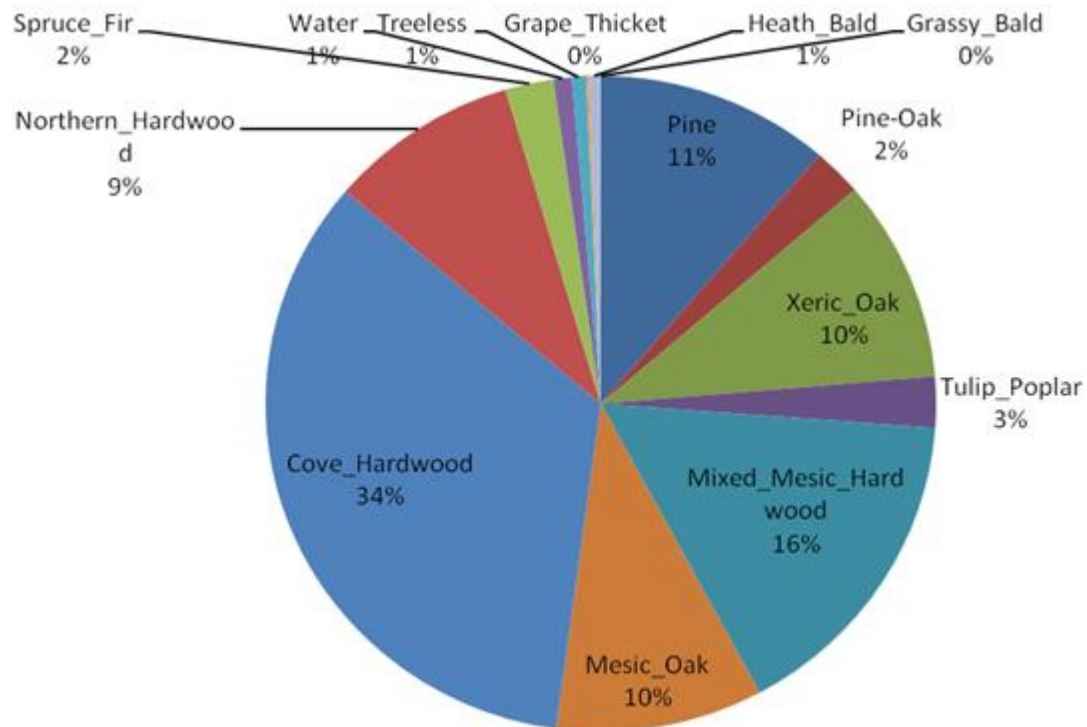


Figure 5.1. The percentage of vegetation types in GRSM.

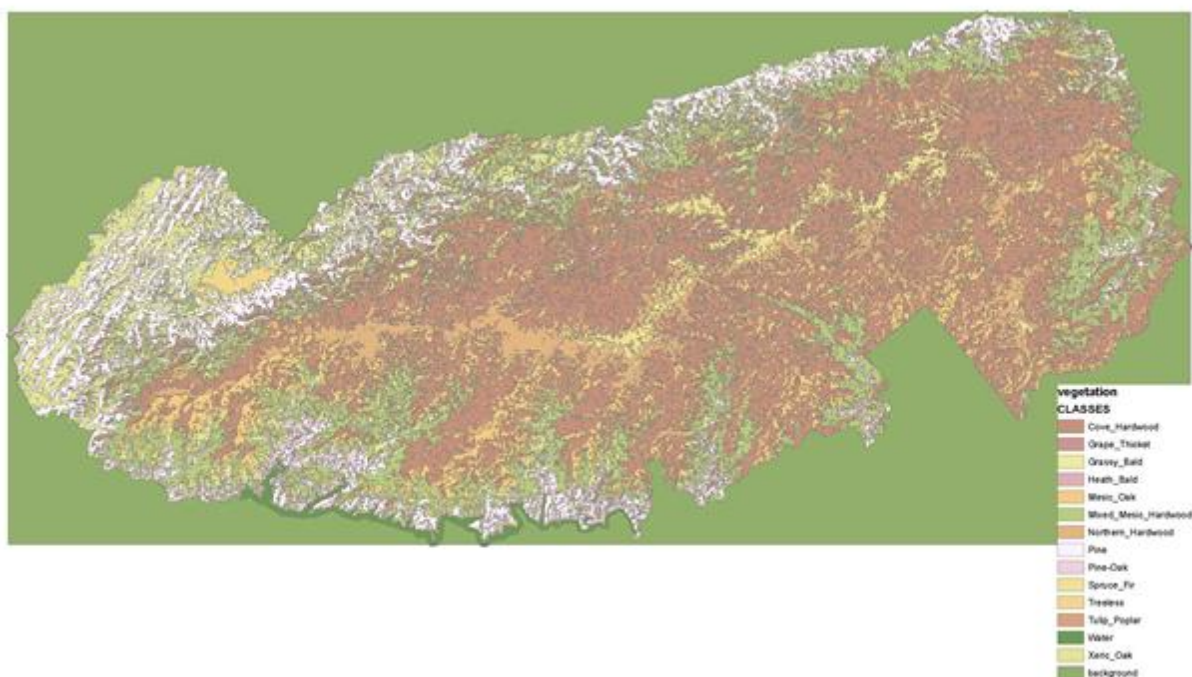


Figure 5.2. Forest\vegetation types in GRSM.

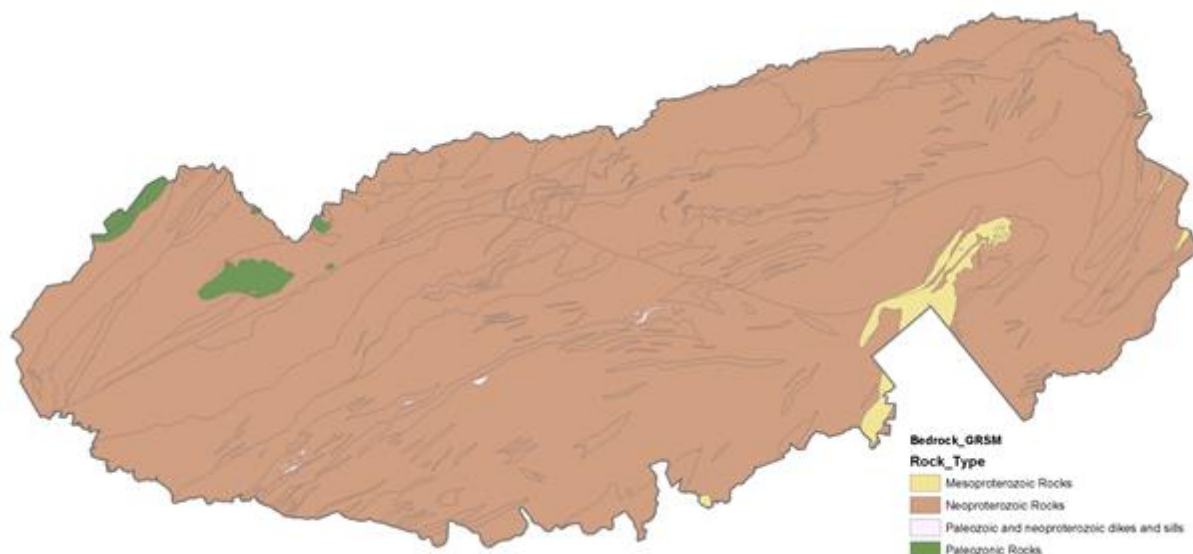


Figure 5.3. GRSM geology map.

Table 5.1. Summary of the soil types in the GRSM.

Soil order	subgroup	Area	% of Area
Entisols	Typic Udifluvents	171252.894	0.01%
	Typic Udipsamments	186086.147	0.01%
	No Subgroup Populated - Soil - Udorthents	205330.718	0.01%
Inceptisols	Cumulic Humaquepts	560734.546	0.03%
	Fluvaquentic Dystrudepts	621880.118	0.03%
	Fluventic Humic Dystrudepts	3441716.81	0.17%
	Humic Dystrudepts	656920217	31.84%
	Humic Lithic Dystrudepts	1567960.42	0.08%
	Lithic Dystrudepts	9491430.76	0.46%
	Oxyaquic Dystrudepts	13813227.3	0.67%
	Typic Dystrudepts	1100468047	53.34%
	No Subgroup Populated - Rubble land	401778.457	0.02%
Ultisols	Aeric Epiaquults	170922.787	0.01%
	Aquic Hapludults	896490.412	0.04%
	Oxyaquic Hapludults	576827.6	0.03%
	Typic Hapludults	250295158	12.13%
	Humic Hapludults	5129605.43	0.25%
Others	No Subgroup Populated - Slide area	2546984.61	0.12%
	No Subgroup Populated - Water	15709344.7	0.76%

Appendix 6. Principal Component Analysis for Soil and Vegetation Variables Analyzed by SAS v.9.

Table 6.1. Principal component analysis for soil type.

Eigenvalues of the Covariance Matrix				
	Eigenvalue	Difference	Proportion	Cumulative
1	0.35383669	0.31355824	0.8967	0.8967
2	0.04027845	0.03982809	0.1021	0.9988
3	0.00045036	0.00041425	0.0011	0.9999
4	0.00003611	0.00003141	0.0001	1.0000
5	0.00000470	0.00000470	0.0000	1.0000
6	0.00000000	0.00000000	0.0000	1.0000
7	0.00000000		0.0000	1.0000

Eigenvectors								
		Prin1	Prin2	Prin3	Prin4	Prin5	Prin6	Prin7
Inceptisols	Inceptisols	0.053938	0.362263	-.097703	0.237648	0.683008	-.577350	-.000000
Ultisols	Ultisols	-.056227	-.360658	0.092477	-.069421	0.721152	0.577350	0.000000
Humic_Dystrudepts	Humic_Dystrudepts	0.429268	0.119312	0.684126	-.010644	0.004385	0.000000	-.577350
Typic_Dystrudepts	Typic_Dystrudepts	-.378008	0.241646	0.682104	-.010471	0.002901	-.000000	0.577350
Typic_Hapludults	Typic_Hapludults	-.054199	-.358443	0.111517	0.918798	-.109341	-.000000	0.000000
Humic_typic_Dys	Humic_typic_Dys	0.807276	-.122335	0.002022	-.000174	0.001484	-.000000	0.577350
Sdif_ept_ult	Sdif_ept_ult	0.110164	0.722922	-.190180	0.307069	-.038143	0.577350	0.000000

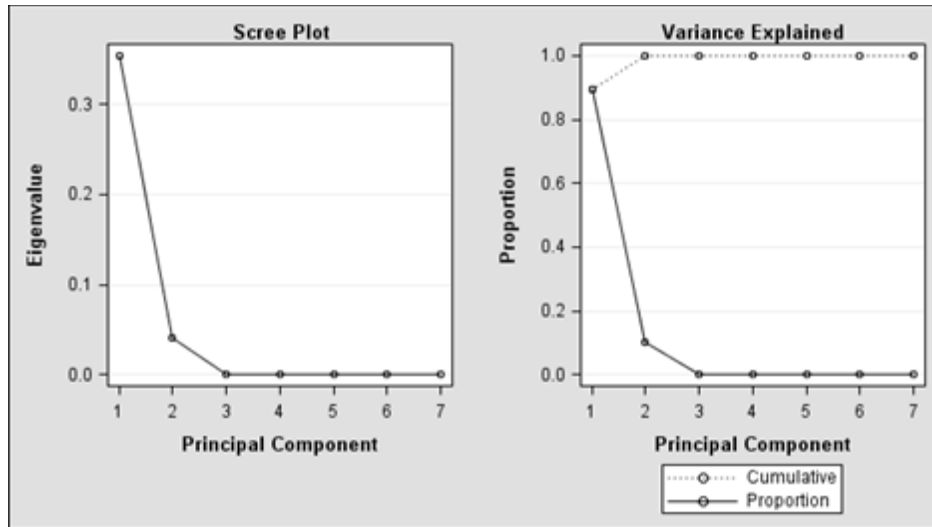
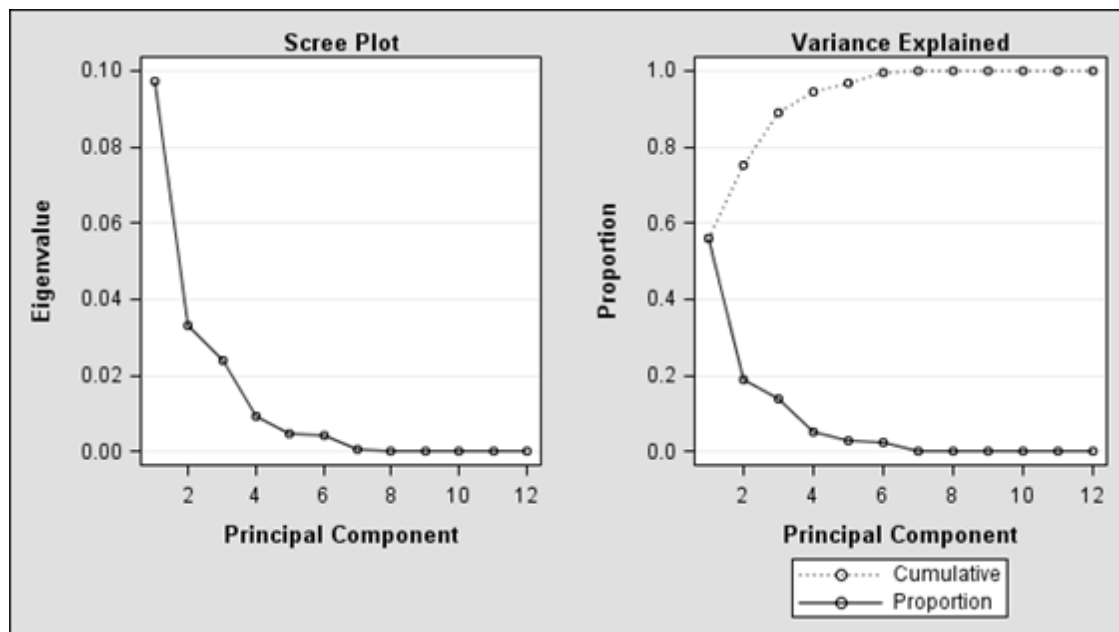


Table 6.2. Principal components analysis for vegetation variables.

Eigenvalues of the Covariance Matrix				
	Eigenvalue	Difference	Proportion	Cumulative
1	0.09718248	0.06411476	0.5605	0.5605
2	0.03306772	0.00904281	0.1907	0.7512
3	0.02402491	0.01482174	0.1386	0.8898
4	0.00920317	0.00458053	0.0531	0.9429
5	0.00462264	0.00017766	0.0267	0.9696
6	0.00444498	0.00401239	0.0256	0.9952
7	0.00043259	0.00021980	0.0025	0.9977
8	0.00021280	0.00002473	0.0012	0.9989
9	0.00018807	0.00018807	0.0011	1.0000
10	0.00000000	0.00000000	0.0000	1.0000
11	0.00000000	0.00000000	0.0000	1.0000
12	0.00000000		0.0000	1.0000



Eigenvectors													
		Prin1	Prin2	Prin3	Prin4	Prin5	Prin6	Prin7	Prin8	Prin9	Prin10	Prin11	Prin12
Cove_Hardwood	Cove_Hardwood	0.407677	-.002667	-.746809	0.070777	0.061825	0.258766	0.187755	0.181547	-.030311	0.045992	0.170389	0.316228
Mesic_Oak	Mesic_Oak	0.146313	0.167973	0.080715	-.057028	0.375119	-.782647	0.060661	0.228908	-.011561	0.045992	0.170389	0.316228
Mixed_Mesic_Hardwood	Mixed_Mesic_Hardwood	-.123834	0.449706	0.194088	-.668397	-.211923	0.255911	0.208322	0.106195	-.042185	0.045992	0.170389	0.316228
Northern_Hardwood	Northern_Hardwood	0.164171	-.751693	0.409200	-.111694	0.111786	0.199024	0.128976	0.162604	-.041911	0.045992	0.170389	0.316228
Pine	Pine	-.263974	0.146845	0.054175	0.105691	0.601642	0.303603	0.072722	0.180711	0.159708	0.344942	0.397573	-.316228
Pine_Oak	Pine_Oak	-.051803	0.021061	0.021506	0.124555	0.099828	-.015433	0.273750	-.803276	0.345476	0.045992	0.170389	0.316228
Spruce_Fir	Spruce_Fir	-.063873	-.244417	-.174775	-.139485	-.525731	-.313487	0.156570	0.083098	0.321002	0.344942	0.397573	-.316228
Tulip_Poplar	Tulip_Poplar	-.021456	0.021839	-.022342	-.014438	-.056378	0.086401	-.821221	0.055836	0.423133	0.045992	0.170389	0.316228
Xeric_Oak	Xeric_Oak	-.186377	0.218541	0.243322	0.692021	-.369373	0.070795	0.165151	0.272328	-.073294	0.045992	0.170389	0.316228
Hardwood	Hardwood	0.334693	0.124760	0.179681	0.035796	0.010884	0.072816	0.203394	0.204142	0.569347	0.321945	-.567962	0.000000
Softwood	Softwood	-.327848	-.097572	-.120600	-.033794	0.075911	-.009885	0.229292	0.263810	0.480710	-.712879	0.000000	0.000000
Vdif	Vdif	0.662540	0.222331	0.300281	0.069590	-.065028	0.082700	-.025899	-.059667	0.088637	-.367938	0.397573	-.316228

Appendix 7. Median Stream Chemistry Values of Baseflow and Stormflow for 387 Stream Survey Sites from 1993 to 2009.

Table 7.1. Median stream chemistry for baseflow. Site ID is same to the Appendix 1 site IDs. Ion units: $\mu\text{eq L}^{-1}$ except pH as standard pH units, conductivity as $\mu\text{S cm}^{-1}$, and metals as mg L^{-1} .

Site ID	N	pH	ANC	Cond	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BCS	Al	Cu	Fe	Mn	Si	Zn
1	36	6.2	35.3	15.4	13.6	24.6	45.8	34.6	0.0	11.0	19.7	70.7	55.1	0.0	0.0	0.0	0.0	2.3	0.0
2	6	6.7	58.0	15.7	11.8	20.5	27.9	32.6	0.0	10.4	20.4	60.9	59.3						
3	34	6.5	73.2	15.4	12.9	13.7	32.5	48.6	0.0	9.9	30.0	69.8	103.8	0.0	0.0	0.0	0.0	3.1	0.0
4	57	6.0	18.5	13.6	11.6	21.4	41.3	31.9	0.0	10.5	23.3	51.2	37.6	0.0	0.0	0.0	0.0	2.2	0.0
5	11	7.0	93.1	18.4	12.6	25.8	38.0	44.9	0.0	7.7	44.3	103.0	126.1						
6	11	6.9	68.9	16.3	12.6	14.2	43.7	34.9	0.0	10.7	47.7	77.5	103.8						
7	5	6.8	94.4	17.0	11.3	6.5	37.9	53.2	0.0	10.1	44.4	72.6	123.9						
8	7	6.9	68.4	17.5	14.6	1.5	66.4	66.3	0.0	15.6	45.3	70.6	113.8						
9	3	7.0	96.3	19.0	14.6	0.0	74.2	51.3	0.0	33.9	55.2	76.8	129.6						
10	4	7.1	162.5	29.5	22.2	0.0	99.1	86.6	0.0	31.4	98.4	136.1	230.9						
11	2	7.1	128.3	31.2	19.2	0.0	126.7	73.7	0.0	12.3	113.0	144.3	197.4						
12	3	6.7	32.4	8.9	11.2	4.7	25.4	29.0	0.0	9.7	22.0	31.0	50.0						
13	56	6.7	108.3	17.5	13.4	6.6	35.0	40.5	0.0	12.4	38.7	79.4	118.9	0.0	0.0	0.0	0.0	2.9	0.0
14	23	6.7	101.6	16.7	14.8	5.6	33.0	43.9	0.0	13.7	35.4	74.7	109.6	0.0	0.0	0.1	0.0	1.0	0.0
15	2	7.1	92.8	18.8	26.2	1.8	41.4	44.5	0.0	11.4	44.6	90.6	121.7						
16	4	7.0	95.9	17.7	18.6	5.0	35.8	37.1	0.0	12.5	28.5	84.6	98.8						
17	10	7.0	103.2	18.0	13.8	7.3	34.5	39.2	0.0	12.4	29.3	93.5	112.6						
18	5	7.0	69.5	11.9	11.8	2.9	26.8	51.9	0.0	18.8	24.4	44.5	103.1						
19	4	6.9	69.1	15.3	17.9	5.9	33.5	41.2	0.0	12.2	26.4	76.2	97.9						
20	31	6.5	90.9	15.8	14.0	8.8	32.9	40.6	0.0	13.1	29.7	84.5	107.0	0.1	0.0	0.0	0.0	1.0	0.0
21	8	7.2	201.1	26.5	14.1	0.0	35.1	74.4	0.0	9.8	75.8	125.4	227.9						
22	7	7.2	141.2	22.6	17.4	4.5	52.2	71.5	0.0	8.8	61.0	100.9	146.7						
23	77	6.7	108.8	17.9	13.5	8.4	31.4	37.1	0.0	11.1	48.0	79.0	122.4	0.0	0.0	0.0	0.0	2.7	0.0
24	58	6.8	143.8	22.4	14.7	5.2	42.6	52.4	0.0	13.2	47.5	102.4	150.8	0.0	0.0	0.0	0.0	3.6	0.0
25	7	7.4	193.7	23.6	18.7	1.0	59.9	63.5	0.0	13.3	74.4	157.1	312.3						
26	5	6.9	85.2	18.9	14.5	11.3	47.0	53.2	0.0	11.8	31.8	96.7	113.0						
27	5	7.2	128.4	23.5	14.1	5.7	21.8	64.3	0.0	10.6	34.6	107.7	162.9						

Site ID	N	pH	ANC	Cond	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BCS	Al	Cu	Fe	Mn	Si	Zn
28	5	6.6	37.2	16.1	13.4	20.2	46.4	29.0	0.0	9.8	26.1	64.0	52.5						
29	15	7.0	97.6	21.0	17.1	17.7	57.4	46.7	0.0	10.0	50.5	121.2	135.5						
30	62	6.5	63.9	20.4	16.7	25.7	63.3	35.6	0.0	9.6	44.1	95.9	78.2	0.0	0.0	0.0	0.0	2.2	0.0
31	5	6.8	75.5	19.2	15.7	14.5	64.4	35.3	0.0	12.6	52.8	112.6	91.3						
32	4	6.8	63.9	17.8	12.7	50.3	43.7	43.7	0.0	16.8	33.3	123.3	98.6						
33	1	6.6	29.0	14.5	15.3	22.8	57.1	27.9	0.0	12.3	23.6	52.8	21.3						
34	24	6.5	66.4	14.6	16.7	9.4	31.0	40.5	0.0	12.5	24.6	61.3	85.8	0.1	0.0	0.0	0.0	3.0	0.0
35	11	6.9	67.9	15.0	13.3	9.0	33.4	35.7	0.0	10.4	25.5	78.7	94.7						
36	5	6.7	42.7	9.3	19.4	3.2	21.7	39.3	0.0	16.2	14.3	29.9	55.6						
37	5	7.0	108.9	19.8	20.9	0.0	54.9	87.6	0.0	23.5	81.1	150.7	180.9						
38	12	6.7	58.4	11.5	13.5	4.2	25.5	36.1	0.0	9.6	18.9	57.9	81.4						
39	6	6.7	41.8	9.3	12.0	5.1	17.4	33.9	0.0	10.1	16.7	56.9	73.8						
40	22	6.8	48.2	13.5	12.3	10.7	33.4	30.8	0.0	9.4	21.5	61.1	65.1						
41	3	6.7	41.1	13.2	12.2	11.4	31.7	32.9	0.0	11.8	20.3	48.8	55.3						
42	15	6.7	41.4	13.6	11.4	11.8	35.0	27.3	0.0	9.7	20.1	58.3	60.9						
43	46	6.0	12.8	15.7	13.9	23.8	58.9	29.1	0.0	6.3	35.3	58.2	30.1	0.0	0.0	0.0	0.0	1.9	0.0
44	7	6.3	11.0	11.3	12.9	32.3	35.8	20.3	0.0	8.0	17.9	50.2	20.6						
45	38	5.6	4.2	18.9	15.7	31.2	82.7	24.3	0.0	4.8	47.7	70.9	13.0	0.1	0.0	0.1	0.0	1.8	0.0
46	33	5.8	7.4	16.2	14.4	26.1	70.5	31.3	0.0	4.5	42.0	58.3	17.0	0.1	0.0	0.0	0.0	2.1	0.0
47	32	6.0	12.2	11.6	14.4	19.9	37.2	26.9	0.0	8.9	20.7	43.4	25.2	0.1	0.0	0.0	0.0	2.0	0.0
48	11	6.6	40.3	16.8	12.6	18.5	55.7	37.0	0.0	8.9	35.2	72.0	72.7						
49	36	6.3	37.9	15.7	13.0	16.7	49.0	34.5	0.0	7.6	30.5	65.9	60.7	0.0	0.0	0.0	0.0	2.3	0.0
50	24	6.4	39.1	14.7	15.4	16.7	44.2	35.4	0.0	9.0	26.6	57.6	49.4	0.1	0.0	0.0	0.0	0.9	0.0
51	5	6.6	51.8	18.1	12.8	14.7	42.3	39.8	0.0	9.8	26.2	61.9	65.9						
52	34	6.4	56.8	15.5	14.3	15.0	45.1	39.1	0.0	8.6	30.3	75.6	77.5	0.0	0.0	0.0	0.0	1.0	0.0
53	7	4.9	-8.3	23.8	15.1	37.2	77.5	24.0	0.0	13.2	21.2	60.9	-15.1						
54	6	6.2	16.8	17.8	17.2	36.6	75.6	25.9	0.0	11.9	29.7	89.5	25.5						
55	8	6.4	22.0	15.0	13.9	31.8	59.2	30.2	0.0	14.4	24.0	85.4	44.3						
56	9	6.5	28.3	17.0	13.2	29.8	60.9	30.2	0.0	13.0	24.4	80.9	33.1						
57	7	6.7	54.3	15.6	13.5	17.3	36.3	35.6	0.0	11.0	25.8	65.2	63.4						
58	8	7.0	87.5	16.9	12.8	11.2	37.2	50.1	0.0	12.6	30.0	94.2	132.9						
59	4	6.3	14.2	16.4	11.9	30.3	63.9	27.4	0.0	10.5	25.5	70.1	41.7						
60	7	5.3	-3.2	20.5	15.8	34.7	73.4	23.0	0.0	10.9	26.1	69.4	-2.7						

Site ID	N	pH	ANC	Cond	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BCS	Al	Cu	Fe	Mn	Si	Zn
61	4	5.1	-3.1	20.7	19.1	40.6	82.4	29.8	0.0	12.4	28.2	70.8	2.5						
62	4	5.1	-5.6	22.8	15.2	47.6	82.3	21.2	0.0	12.6	26.0	70.2	-16.6						
63	5	5.0	-3.8	20.2	16.9	40.0	75.5	37.2	0.0	10.8	22.9	62.1	3.3						
64	4	6.2	16.6	18.6	14.9	28.1	62.2	33.1	0.0	11.0	21.7	73.3	34.4						
65	2	6.7	43.9	17.6	17.7	27.9	63.1	31.5	1.7	12.2	36.8	84.6	56.4						
66	78	6.3	39.8	19.7	15.2	32.9	68.7	26.6	0.0	7.0	45.5	96.7	57.6	0.0	0.0	0.0	0.0	1.8	0.0
67	5	6.3	40.5	26.3	15.2	29.0	119.3	22.0	0.0	9.0	55.1	121.5	56.5						
68	7	6.4	25.7	19.8	14.1	34.6	66.0	26.5	0.0	6.5	44.6	93.7	62.4						
69	12	5.7	0.8	17.4	17.4	44.1	60.7	22.8	0.0	3.9	49.1	60.0	12.0						
70	7	6.4	27.0	16.2	12.5	36.7	44.0	31.8	0.0	9.8	28.4	78.6	56.7						
71	58	6.2	28.7	15.9	13.9	33.0	44.4	28.1	0.0	8.8	28.6	70.7	44.1	0.0	0.0	0.0	0.0	2.1	0.0
72	34	6.5	26.0	16.3	13.3	32.3	44.6	26.5	0.0	7.1	28.3	77.7	48.8						
73	62	6.4	36.3	20.9	16.2	33.3	78.7	25.5	0.0	5.8	49.1	101.2	50.9	0.0	0.0	0.0	0.0	1.6	0.0
74	63	6.5	63.9	25.6	16.6	34.5	89.8	27.9	0.0	5.0	53.5	127.4	75.9	0.0	0.0	0.0	0.0	1.7	0.0
75	19	5.0	-7.9	18.2	13.7	34.4	73.1	15.6	0.0	3.2	42.9	47.3	-9.5						
76	14	5.1	-8.1	18.9	13.1	35.2	74.8	16.1	0.0	3.2	46.0	48.6	-10.2						
77	12	6.3	15.1	16.2	12.9	43.2	56.6	16.3	0.0	3.3	59.7	67.5	28.0						
78	3	6.4	26.4	21.3	19.0	16.8	116.5	20.1	1.1	8.2	69.6	120.5	66.1						
79	24	4.7	-17.9	21.9	13.4	34.9	84.6	16.2	0.0	3.2	37.1	43.1	-31.9						
80	10	5.1	-5.6	18.1	11.5	33.5	70.0	19.3	0.0	4.2	32.4	53.7	-4.6						
81	7	6.1	16.1	16.5	11.1	36.1	62.1	24.9	0.0	6.1	38.9	71.1	42.0						
82	10	6.3	27.0	13.6	15.3	20.8	32.2	25.2	0.0	3.5	21.3	52.1	38.4						
83	5	6.4	27.1	14.2	13.3	19.9	43.5	35.4	0.0	10.7	24.9	67.2	53.9						
84	12	6.4	22.1	14.6	13.1	27.2	44.7	33.5	0.0	10.8	23.5	63.0	43.6						
85	1	6.5	46.0	9.5	14.1	8.9	37.5	39.6	0.0	25.5	22.7	64.0	91.4						
86	11	6.2	15.6	14.2	13.0	32.7	44.9	32.0	0.0	9.7	21.6	55.3	28.3						
87	11	6.3	15.4	14.6	12.9	28.3	47.9	29.6	0.0	8.9	23.9	54.5	28.5						
88	11	6.2	15.3	13.9	13.0	27.3	39.9	30.3	0.0	9.8	18.4	47.9	27.0						
89	8	6.0	9.9	13.0	13.7	28.4	38.3	27.3	0.0	10.9	19.6	45.2	20.3						
90	5	5.2	1.2	15.0	16.4	42.4	40.9	28.5	0.0	11.0	18.8	58.1	22.2						
91	8	6.2	17.2	13.9	15.4	33.9	38.8	31.6	0.0	9.5	21.8	54.5	35.4						
92	22	4.8	-14.8	19.5	15.9	37.7	55.2	30.9	0.0	9.9	15.6	37.3	-0.7						
93	15	5.1	-6.5	18.0	13.6	44.0	44.9	28.1	0.0	9.7	17.0	46.5	2.5						

Site ID	N	pH	ANC	Cond	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BCS	Al	Cu	Fe	Mn	Si	Zn
94	2	4.9	-11.0	23.6	13.3	41.8	40.2	25.3	0.0	7.5	16.5	41.9	-3.9						
95	1	5.0	-8.6	24.1	15.1	46.2	41.3	8.6	0.0	6.3	28.2	84.0	24.5						
96	9	6.0	5.0	16.4	17.3	38.6	53.2	37.9	0.0	9.5	26.7	58.5	22.2						
97	3	6.4	14.3	15.3	10.9	29.4	50.1	39.1	0.0	10.0	30.5	73.9	70.2						
99	3	6.2	20.8	8.5	14.1	8.5	24.9	25.8	0.0	7.3	14.0	34.7	39.1						
100	2	7.1	92.5	15.4	15.4	11.8	21.7	58.8	0.0	15.8	32.5	75.3	133.5						
101	2	6.5	21.8	11.3	14.8	32.5	17.1	37.3	0.0	10.9	18.4	39.6	43.5						
102	2	6.1	9.5	11.9	13.2	36.0	24.4	36.1	0.0	10.4	20.8	39.4	33.2						
103	46	5.6	2.3	18.9	14.4	47.4	66.6	28.9	0.0	10.7	22.8	83.8	19.0	0.1	0.0	0.0	0.0	2.0	0.0
104	38	5.7	6.5	17.9	14.9	49.7	55.3	29.5	0.0	12.6	19.8	72.9	17.2	0.0	0.0	0.0	0.0	2.2	0.0
105	16	5.8	2.5	18.3	11.8	39.9	58.8	22.6	0.0	11.7	20.1	80.3	8.2						
106	37	6.0	15.5	17.0	14.2	40.2	57.6	28.7	0.0	13.0	21.9	83.8	34.1	0.0	0.0	0.0	0.0	2.2	0.0
107	54	6.1	19.6	16.0	11.9	33.4	53.2	29.4	0.0	11.2	20.0	71.4	33.8	0.1	0.0	0.0	0.0	2.2	0.0
108	2	6.1	7.6	15.7	15.4	20.4	65.7	27.8	0.0	6.1	31.1	61.7	25.1						
109	2	6.1	14.2	17.8	16.6	28.2	78.6	23.8	0.0	7.3	43.4	91.8	42.8						
110	10	5.4	1.6	18.0	19.1	67.4	18.3	32.4	0.0	6.8	24.4	44.7	0.1						
111	13	6.7	39.5	13.0	9.9	26.9	13.7	33.4	0.0	6.0	16.5	53.7	62.3						
112	6	4.4	-25.6	26.2	12.8	36.6	69.1	30.3	0.0	7.2	9.1	30.3	-44.8						
113	7	4.5	-28.3	23.9	10.5	52.6	58.4	24.4	0.0	6.8	6.7	34.0	-45.0						
114	51	6.3	35.5	16.9	13.6	38.7	46.8	34.2	0.0	8.7	34.6	66.2	45.5	0.0	0.0	0.0	0.0	2.3	0.0
115	25	6.2	35.6	16.2	16.1	27.7	48.5	33.0	0.0	8.2	34.7	64.3	50.0	0.1	0.0	0.0	0.0	2.2	0.0
116	2	6.7	30.5	14.8	16.3	21.3	14.8	31.3	0.0	8.5	25.1	46.3	58.7						
117	4	6.4	60.2	14.5	14.1	15.5	26.2	46.8	0.0	11.0	20.2	64.7	82.8						
118	5	6.4	23.2	12.1	9.0	8.1	38.6	33.9	0.0	4.7	16.3	33.0	35.8						
119	2	6.6	78.1	14.5	10.4	20.3	18.4	39.4	0.0	7.1	28.0	69.2	94.7						
120	3	6.4	37.8	12.5	9.8	18.4	40.8	22.8	0.0	6.7	25.1	48.1	34.4						
121	6	6.6	69.6	15.6	11.3	4.8	44.3	34.9	0.0	9.4	43.6	74.3	92.4						
122	3	6.4	36.8	16.3	11.7	22.6	44.2	25.2	0.0	9.2	31.7	55.7	41.1						
123	5	6.6	47.4	13.2	13.5	13.0	29.5	28.9	0.0	6.5	36.5	50.5	56.3						
124	5	6.7	55.7	13.2	16.1	20.4	20.7	36.4	0.0	5.8	38.4	48.5	67.4						
125	10	7.0	84.8	12.1	12.2	5.9	9.4	47.7	0.0	12.5	17.9	53.8	105.2						
126	11	6.6	33.2	14.5	15.9	52.1	5.2	39.5	0.0	11.9	15.3	47.6	37.4						
127	36	6.4	46.9	11.2	15.5	14.6	19.4	39.5	0.0	11.2	18.4	42.2	56.7	0.1	0.0	0.0	0.0	2.4	0.0

Site ID	N	pH	ANC	Cond	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BCS	Al	Cu	Fe	Mn	Si	Zn
128	10	6.8	49.5	10.4	16.0	20.8	15.0	39.2	0.0	13.3	21.9	52.0	86.2						
129	11	6.8	44.0	10.8	15.9	21.8	16.1	35.5	0.0	10.9	22.1	50.1	70.0						
130	11	6.7	43.2	12.0	22.2	27.4	20.0	44.3	0.0	15.7	20.8	45.6	52.1						
131	11	6.7	42.4	14.3	16.6	24.0	34.1	34.8	0.0	12.9	22.5	57.8	52.8						
132	10	6.6	38.0	11.8	12.8	14.8	27.8	33.1	0.0	10.3	24.2	54.0	68.9						
133	12	6.8	46.4	14.1	13.3	20.6	37.8	39.5	0.0	9.0	35.7	63.3	77.6						
134	20	6.9	57.7	16.4	11.8	19.9	44.0	32.7	0.0	9.4	39.1	68.5	72.8						
135	9	6.9	58.2	16.2	14.4	19.5	47.5	36.6	0.0	8.4	47.2	68.6	69.3						
136	6	6.4	28.5	7.4	15.8	3.2	14.4	28.2	0.0	13.6	17.9	20.1	46.1						
137	63	5.9	11.4	14.5	13.3	30.6	51.4	29.8	0.0	8.4	25.4	53.7	24.4	0.0	0.0	0.0	0.0	2.3	0.0
138	37	5.6	3.0	13.8	15.6	33.1	38.2	28.5	0.0	8.9	18.5	47.6	19.4	0.1	0.0	0.0	0.0	2.4	0.0
139	4	6.4	24.2	8.7	14.8	12.0	18.1	25.6	0.0	4.9	8.4	33.3	29.1						
140	15	6.8	45.6	11.3	12.0	11.5	17.1	30.5	0.0	9.8	20.3	40.9	62.4						
141	16	6.9	65.1	10.8	12.0	5.9	13.0	35.5	0.0	11.5	18.0	51.7	88.0						
142	62	6.5	56.6	11.0	12.0	7.9	15.7	36.0	0.0	12.3	17.4	38.3	68.7	0.0	0.0	0.0	0.0	2.8	0.0
143	64	6.4	47.8	10.7	12.3	8.6	21.3	35.9	0.0	11.2	16.3	36.0	55.8	0.0	0.0	0.0	0.0	2.6	0.0
144	64	6.5	51.4	11.3	11.9	8.9	18.4	36.8	0.0	11.5	17.6	38.1	60.2	0.0	0.0	0.0	0.0	2.7	0.0
145	5	6.7	66.4	11.7	14.1	11.5	20.5	43.3	0.0	13.5	22.0	50.0	76.7						
146	13	6.9	59.2	11.1	11.3	9.9	17.9	39.3	0.0	11.1	20.9	57.1	90.9						
147	76	6.6	84.5	14.7	13.2	9.7	21.3	47.9	0.0	15.1	26.5	52.5	97.6	0.0	0.0	0.0	0.0	3.5	0.0
148	60	6.7	124.5	16.8	12.3	5.7	19.8	67.2	0.0	15.7	30.0	61.5	134.3	0.0	0.0	0.0	0.0	4.5	0.0
149	58	6.6	79.1	14.3	12.6	10.6	21.3	48.3	0.0	13.6	25.8	49.6	91.5	0.0	0.0	0.0	0.0	3.5	0.0
150	29	6.6	79.2	14.1	15.1	9.0	19.9	49.1	0.0	13.5	24.8	50.8	90.6	0.1	0.0	0.0	0.0	3.6	0.0
151	14	7.1	122.3	22.9	15.5	0.0	56.7	57.0	0.0	21.9	86.5	83.7	185.2						
152	22	7.9	629.3	67.5	16.8	5.2	37.5	55.4	0.0	17.0	130.9	530.5	784.2						
153	10	7.8	455.8	59.6	20.6	3.9	40.5	53.0	0.0	15.6	127.4	530.4	687.4						
154	1	6.7	62.9	13.3	24.3	0.0	39.1	36.8	2.0	11.5	20.7	28.1	33.7						
155	1	6.5	27.8	11.8	17.5	17.6	22.5	21.9	0.0	6.5	10.5	30.9	12.2						
156	28	7.3	525.7	52.5	20.8	1.8	43.4	56.1	0.0	16.9	133.8	472.0	629.2						
157	4	7.0	161.9	18.9	17.1	0.0	15.6	43.4	0.0	14.0	54.3	102.4	176.8						
158	7	6.8	44.7	10.3	15.1	6.1	20.3	36.3	0.0	11.1	16.3	51.6	71.0						
159	5	7.2	138.3	18.2	15.0	0.0	24.2	60.7	0.0	20.3	50.4	96.4	162.0						
160	6	7.7	412.1	43.4	18.6	2.0	47.5	59.3	0.0	19.5	108.4	187.1	131.0						

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161	5	7.0	74.5	14.9	17.5	0.0	30.1	56.5	0.0	15.5	27.8	59.3	111.3						
162	5	7.3	192.3	25.7	17.2	0.0	35.5	63.2	0.0	19.6	74.5	130.5	215.6						
163	2	7.2	158.9	44.0	20.2	0.6	213.4	74.5	0.1	17.5	145.4	165.2	168.4						
164	2	7.1	103.3	20.5	13.3	0.0	57.1	46.0	0.0	15.4	71.0	69.4	131.5						
165	2	6.9	102.5	20.1	26.7	0.0	45.5	62.7	0.0	22.1	57.9	69.5	140.1						
166	2	7.1	83.5	21.5	23.8	1.8	68.5	76.0	0.0	27.9	47.5	64.6	121.9						
167	2	7.0	73.6	14.4	14.7	0.0	35.2	57.1	0.0	22.1	32.0	50.1	111.4						
168	2	6.6	69.6	18.1	14.7	0.7	63.7	41.6	0.0	9.6	44.8	55.2	72.0						
169	2		346.4	41.7	19.3	3.3	59.1	74.7	0.0	13.7	110.1	229.1	346.0						
170	2	6.6	78.8	18.3	18.5	0.8	67.6	43.0	0.0	11.5	50.9	67.3	85.7						
171	1	7.4	586.6	77.9	42.4	0.0	99.8	47.5	0.0	34.7	130.9	709.7	780.4						
172	2	6.9	119.3	20.2	26.6	4.9	29.7	65.8	0.0	18.8	50.0	107.5	180.9						
173	61	6.8	110.9	17.8	15.9	7.5	26.0	44.4	0.0	12.1	46.4	84.9	133.8	0.0	0.0	0.0	0.0	3.1	0.0
174	59	7.6	1109.4	118.2	20.5	12.4	51.7	54.4	0.0	15.3	208.1	882.8	1081.2	0.0	0.0	0.0	0.0	3.5	0.0
175	14	7.0	94.7	21.8	15.4	0.0	68.6	63.2	0.0	32.2	55.3	79.6	159.1						
176	15	7.7	464.1	52.8	16.9	2.7	53.3	54.7	0.0	23.5	107.1	387.4	486.5						
177	7	6.6	44.6	10.8	14.0	6.4	21.7	34.8	0.0	9.4	18.5	55.6	82.0						
178	4	6.3	23.9	10.2	16.0	10.5	12.8	28.3	0.0	7.4	11.7	28.1	30.2						
179	3	6.7	39.7	8.9	12.1	6.5	20.1	24.3	0.0	9.5	15.2	31.3	42.7						
180	2	6.7	41.0	8.2	11.3	2.2	13.7	23.4	0.0	6.9	11.4	27.3	41.8						
181	4	6.6	43.3	9.7	11.7	4.0	18.2	22.9	0.0	7.2	13.4	30.0	40.6						
182	2	6.7	40.4	11.1	15.5	21.3	7.1	25.7	0.0	4.6	13.1	30.7	30.1						
183	32	5.8	35.8	9.2	13.9	5.0	8.6	31.1	0.0	6.5	11.4	22.4	41.4	0.2	0.0	0.2	0.0	1.9	0.1
184	37	6.2	34.2	12.7	18.2	24.7	26.5	39.5	0.0	11.3	18.0	47.6	50.4	0.1	0.0	0.0	0.0	1.5	0.0
185	13	6.7	41.6	13.2	15.3	19.3	28.6	39.7	0.0	10.7	20.0	64.9	71.5						
186	47	6.4	49.9	13.1	16.4	17.1	27.5	41.9	0.0	11.5	22.1	54.9	71.0	0.1	0.0	0.0	0.0	2.4	0.0
187	6	7.0	78.2	20.3	17.5	2.9	41.7	47.2	0.0	8.9	44.1	93.6	107.4						
188	6	6.7	35.5	8.7	12.3	0.0	17.3	32.5	0.0	7.0	12.5	42.2	61.8						
189	7	6.6	36.4	10.2	14.7	4.1	27.9	30.1	0.0	9.3	18.9	52.9	58.3						
190	29	6.3	34.3	11.9	14.6	15.7	30.4	32.8	0.0	8.7	17.9	42.3	46.6	0.1	0.0	0.0	0.0	0.8	0.0
191	31	6.1	19.5	10.7	15.5	18.0	24.9	30.6	0.0	9.0	16.1	36.7	38.4	0.1	0.0	0.0	0.0	2.0	0.0
192	33	6.1	23.6	12.7	13.7	21.6	40.4	28.2	0.0	6.8	23.3	52.3	33.8	0.1	0.0	0.0	0.0	1.9	0.0
193	46	6.4	54.9	11.6	14.8	6.5	23.3	36.9	0.0	10.1	22.6	47.3	67.7	0.1	0.0	0.1	0.0	1.0	0.0

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194	31	6.4	45.7	11.9	15.5	9.4	27.6	36.0	0.0	9.3	23.3	45.9	59.0	0.0	0.0	0.0	0.0	0.9	0.0
195	29	5.8	29.8	7.6	15.5	3.3	8.5	25.3	0.0	6.0	9.5	18.6	34.3	0.1	0.0	0.0	0.0	1.4	0.0
196	4	6.6	34.5	12.9	17.9	16.3	16.5	35.5	1.5	12.3	13.8	33.0	57.3						
197	3	6.5	29.4	8.9	12.2	12.9	22.7	21.7	0.0	7.1	16.2	33.3	25.9						
198	3	6.7	40.9	10.1	12.7	7.9	21.4	24.8	0.0	8.3	16.0	34.5	54.3						
199	5	6.9	88.3	15.6	16.9	8.0	22.4	50.6	0.0	14.5	23.7	71.0	118.5						
200	37	6.2	27.3	12.4	17.4	25.9	26.4	36.6	0.0	10.4	16.2	45.4	41.6	0.0	0.0	0.0	0.0	1.1	0.0
201	33	5.8	35.2	10.2	12.0	10.7	15.3	28.1	0.0	9.6	13.8	34.0	46.7	0.1	0.0	0.0	0.0	1.6	0.0
202	1	5.7	0.7	8.8	11.7	14.2	28.9	19.2	0.0	8.6	12.9	34.7	20.6						
203	1	6.8	66.4	14.8	12.9	0.0	41.0	35.0	0.0	13.1	26.3	70.1	90.5						
204	1	6.7	76.9	16.1	9.8	5.0	41.4	34.5	0.0	10.6	26.6	79.6	95.0						
205	2	6.7	49.8	15.4	12.1	0.0	42.7	37.4	0.0	12.8	24.5	62.1	82.0						
207	4	6.6	41.4	8.8	12.2	8.3	13.4	28.1	0.0	8.8	13.9	37.9	52.7						
208	6	6.6	39.0	8.8	13.5	0.0	13.1	35.4	0.0	7.0	13.4	40.0	64.2						
209	31	6.3	35.8	10.3	13.9	4.7	23.6	34.3	0.0	9.6	17.5	32.8	51.5	0.1	0.0	0.0	0.0	3.2	0.0
210	33	6.4	50.0	14.5	12.4	13.9	38.8	33.2	0.0	10.5	22.5	63.5	62.3	0.2	0.0	0.0	0.0	2.5	0.0
211	16	6.7	42.9	12.0	13.3	15.2	28.5	33.2	0.0	9.4	20.3	51.6	59.6						
212	17	6.6	33.6	11.8	12.6	17.1	27.5	29.4	0.0	9.1	20.3	48.4	50.1						
213	31	6.2	20.7	11.2	13.8	19.6	29.1	30.1	0.0	8.3	19.4	37.4	34.2	0.0	0.0	0.0	0.0	2.4	0.0
214	35	6.3	39.2	11.1	15.8	13.3	22.3	34.8	0.0	9.4	18.4	36.3	48.8	0.2	0.0	0.1	0.0	3.0	0.0
215	33	6.4	51.2	14.0	15.1	11.8	35.4	38.5	0.0	9.1	26.5	51.1	60.9	0.0	0.0	0.0	0.0	3.1	0.0
216	5	6.5	31.0	9.5	16.6	20.3	24.6	25.2	0.0	9.4	15.6	45.9	31.3						
218	39	5.1	2.3	20.6	18.0	56.6	58.1	27.3	0.0	13.6	23.4	49.4	-15.8						
219	30	4.9	0.1	23.9	17.0	77.7	61.8	28.1	0.0	13.6	20.9	51.8	-38.7						
220	30	5.4	5.0	16.6	12.8	54.4	32.8	26.2	0.0	11.9	19.7	51.2	8.5						
221	31	6.3	28.8	10.7	13.9	23.8	16.2	32.5	0.0	10.1	17.3	31.4	38.8	0.0	0.0	0.0	0.0	2.5	0.0
222	4	6.7	35.9	9.9	13.5	17.7	16.3	30.5	0.0	9.6	19.0	38.6	51.3						
223	6	6.8	51.0	10.3	14.3	8.4	14.2	35.2	0.0	9.1	18.6	42.9	76.7						
224	6	6.6	48.7	10.7	10.8	13.5	16.3	34.4	0.0	10.8	17.4	34.4	54.0	0.0	0.0	0.0	0.0	2.8	0.0
225	4	6.5	20.1	13.1	17.8	24.5	43.7	28.8	0.0	12.9	20.0	74.4	56.6						
226	4	6.4	20.2	11.5	13.8	10.4	34.2	26.1	0.0	10.9	15.2	52.4	51.7						
227	5	6.3	19.4	11.2	13.1	13.2	36.3	27.8	0.0	8.6	16.5	50.5	52.0						
228	4	6.5	35.9	11.1	14.6	10.5	33.1	31.2	1.1	11.6	20.0	58.9	69.3						

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229	4	6.5	44.5	10.1	14.0	0.0	21.0	34.1	0.0	12.9	21.6	58.4	82.0						
230	3	6.5	45.8	11.2	11.8	0.0	25.7	33.0	0.6	11.7	18.9	48.3	72.3						
231	4	6.5	47.3	9.8	13.3	5.3	22.5	27.5	0.0	9.1	21.1	36.4	51.2						
232	7	6.5	46.5	23.4	17.6	41.6	120.3	24.2	0.0	4.9	46.9	139.1	61.5						
233	55	6.2	36.5	24.5	16.9	33.7	106.0	25.9	0.0	4.3	57.2	119.2	45.9	0.1	0.0	0.0	0.0	1.5	0.0
234	49	5.9	15.7	16.0	13.8	55.4	28.8	32.4	0.0	7.2	28.6	54.9	23.1	0.0	0.0	0.0	0.0	2.3	0.0
235	10	6.2	15.1	16.7	13.5	43.6	41.2	26.8	0.0	8.5	26.0	67.3	47.3						
236	13	5.6	0.5	19.5	13.8	34.9	77.4	23.4	0.0	3.4	49.3	69.9	30.0						
237	66	4.8	-14.6	19.5	13.0	34.0	72.2	18.7	0.0	3.8	32.3	49.7	-11.8	0.1	0.0	0.0	0.0	1.4	0.0
242	12	5.3	3.5	20.8	14.1	46.0	45.6	27.4	0.0	9.1	17.7	32.5	-14.7						
243	18	5.6	3.8	16.0	11.7	38.3	55.9	22.9	0.0	8.4	20.4	72.3	18.2						
244	12	5.9	5.3	15.0	14.5	44.4	41.2	24.8	0.0	8.4	20.5	68.1	22.1						
245	13	6.7	40.3	7.0	11.7	0.0	6.3	35.2	0.0	8.0	10.3	22.2	58.5						
246	11	6.6	29.7	11.0	13.0	19.9	21.6	30.5	0.0	8.4	17.7	47.3	42.9						
247	10	6.6	35.0	10.4	12.4	14.7	16.9	33.7	0.0	8.3	17.6	45.9	67.3						
248	10	6.7	42.3	10.2	13.0	12.4	17.3	33.6	0.0	8.9	18.1	44.0	65.5						
249	5	7.0	68.8	10.5	11.9	0.0	9.7	40.2	0.0	12.2	21.1	43.4	92.1						
250	7	6.6	44.7	15.6	15.1	20.0	53.4	35.6	0.0	10.2	32.6	62.5	48.8						
251	73	6.1	23.4	31.4	17.9	37.9	169.6	42.6	0.0	10.6	81.1	125.6	38.0	0.0	0.0	0.0	0.0	2.7	0.0
252	61	5.0	-3.2	46.0	16.2	52.9	297.6	46.7	0.0	12.0	121.7	135.6	-37.7	0.5	0.0	0.0	0.3	3.4	0.0
253	60	6.5	85.8	24.3	16.8	57.6	42.3	53.3	0.0	9.3	50.6	108.5	100.3	0.0	0.0	0.0	0.0	3.4	0.0
254	5	6.9	58.7	14.5	16.0	43.6	12.5	50.5	0.0	10.5	29.8	90.4	109.9						
255	4	6.8	68.4	12.5	13.3	19.6	11.1	44.7	0.0	11.1	24.7	61.2	98.1						
256	5	6.6	52.1	11.3	11.4	18.1	18.0	37.6	0.0	8.6	21.9	48.1	82.8						
257	3	6.8	49.9	12.0	11.6	16.8	18.5	29.5	0.0	7.3	18.3	47.5	53.4						
258	8	6.8	58.6	10.7	12.9	4.8	17.2	36.9	0.0	8.9	20.9	49.1	82.1						
259	3	6.6	57.2	10.6	11.5	6.3	18.1	37.5	0.0	10.5	23.0	53.8	88.8						
260	5	6.7	43.1	10.0	11.2	6.1	23.3	29.0	0.0	8.0	17.2	46.0	50.2						
261	8	6.6	42.5	9.6	10.3	5.7	21.7	29.7	0.0	7.2	16.7	37.2	54.9						
262	5	6.7	39.0	8.6	9.8	8.2	25.1	27.2	0.0	5.7	17.3	37.7	46.6						
263	5	6.4	25.0	10.7	13.0	10.8	31.4	31.4	0.0	7.9	18.4	41.3	19.1						
264	3	6.2	17.8	10.7	15.7	3.3	22.3	31.6	0.0	7.9	12.0	30.5	39.9						
265	11	6.7	58.6	9.8	13.6	0.0	9.8	34.8	0.0	11.6	15.1	28.0	71.9						

Site ID	N	pH	ANC	Cond	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BCS	Al	Cu	Fe	Mn	Si	Zn
266	31	6.5	71.5	13.7	15.6	5.4	25.4	44.7	0.0	12.5	23.4	47.9	79.5	0.0	0.0	0.0	0.0	2.8	0.0
267	17	7.0	76.4	15.3	16.3	16.5	20.8	50.7	0.0	13.5	22.1	68.8	98.3						
268	59	6.5	64.0	13.5	12.6	9.4	29.9	42.1	0.0	11.2	25.4	49.8	74.3	0.0	0.0	0.0	0.0	3.1	0.0
269	8	6.8	49.3	12.8	15.1	7.2	27.3	33.8	0.0	10.0	22.0	47.5	59.2						
270	23	6.5	45.1	12.8	10.0	12.1	31.0	33.1	0.0	8.8	22.5	43.9	52.6	0.0	0.0	0.0	0.0	2.6	0.0
271	8	6.9	76.3	11.1	10.6	3.8	14.5	42.9	0.0	12.5	18.2	54.8	89.7						
272	6	6.9	78.5	13.0	17.5	4.2	12.3	57.8	0.0	12.0	21.6	63.4	103.2						
273	3	6.7	60.9	10.6	13.6	9.6	9.2	35.6	0.0	12.1	16.6	42.9	66.0						
274	3	6.8	45.5	9.1	12.0	2.5	8.5	22.2	0.0	8.4	12.6	48.3	70.4						
275	3	6.8	70.5	9.2	13.3	1.4	9.8	37.4	0.0	11.6	28.1	46.8	99.8						
276	14	6.7	32.5	11.2	14.1	24.5	14.9	34.6	0.0	9.0	17.0	45.9	49.4						
277	22	6.5	26.4	11.7	13.1	26.8	23.0	38.7	0.0	8.7	17.5	46.5	49.4						
278	7	6.9	62.8	9.1	13.2	4.3	7.3	40.3	0.0	9.3	13.9	46.6	80.9						
279	12	6.9	69.3	10.9	12.0	4.0	7.9	42.2	0.0	10.1	14.7	52.4	69.2						
280	8	6.6	38.1	13.6	14.1	15.5	41.3	35.1	0.0	7.9	29.4	61.8	62.8						
281	9	6.8	48.7	13.1	14.3	12.7	34.5	37.5	0.0	10.1	29.1	61.9	84.5						
282	10	6.8	76.8	11.8	11.8	3.4	19.4	48.6	0.0	12.2	25.0	49.4	104.5						
283	9	6.9	70.2	13.0	14.2	7.8	26.5	45.2	0.0	12.1	26.2	60.8	99.9						
284	4	6.5	30.2	14.5	12.8	20.9	47.9	40.0	1.2	9.8	35.2	66.4	66.9						
285	4	6.9	111.3	17.6	17.9	5.0	18.9	57.0	0.0	15.9	43.1	100.8	165.7						
286	5	6.7	74.8	14.8	16.0	23.3	23.9	49.2	0.0	14.4	29.9	72.0	132.1						
287	5	6.9	93.2	16.0	17.4	10.1	22.5	52.9	0.2	15.1	31.3	61.3	109.3						
288	10	6.9	74.3	12.9	12.0	12.8	13.5	44.7	0.0	9.8	17.7	55.6	91.1						
289	18	6.8	53.3	13.1	13.0	21.2	24.9	41.8	0.0	12.2	19.0	65.6	84.9						
290	13	5.0	-5.4	14.6	14.2	51.8	16.7	28.4	0.0	6.6	20.5	31.9	0.2	0.1	0.0	0.0	0.0	1.9	0.0
291	32	6.2	25.2	12.3	16.1	34.4	22.1	36.7	0.0	9.5	19.4	43.4	35.7	0.1	0.0	0.0	0.0	2.6	0.1
292	11	6.8	59.8	12.8	12.1	16.6	24.2	39.2	0.0	11.2	17.7	59.8	78.0						
293	89	6.6	83.9	16.6	13.5	20.1	24.7	51.9	0.0	14.0	31.7	60.2	95.8	0.0	0.0	0.0	0.0	3.5	0.0
294	7	6.8	65.7	13.1	13.9	13.9	19.6	46.3	0.0	12.7	26.1	59.7	83.3						
295	5	6.7	68.8	14.4	12.8	5.9	19.3	45.5	0.0	13.5	30.6	48.9	92.5						
296	4	6.7	89.0	13.7	12.4	4.3	23.2	43.4	0.0	13.1	26.5	63.8	92.8						
297	4	6.7	67.2	13.3	17.3	11.8	21.0	44.8	0.0	13.9	25.9	48.6	87.1						
298	8	7.5	239.1	27.7	17.5	0.0	35.9	61.7	0.0	19.1	103.0	190.7	299.5						

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299	13	6.9	67.9	11.4	14.4	2.2	15.5	41.7	0.0	12.6	20.3	51.8	89.0						
300	6	6.8	61.7	10.0	11.3	0.0	13.5	36.1	0.0	9.6	17.3	42.5	76.1						
301	7	6.8	53.9	9.5	12.5	2.4	15.8	28.4	0.0	9.9	18.5	53.8	90.0						
302	4	6.8	61.0	10.1	11.9	0.0	16.4	31.9	0.0	9.9	18.5	42.2	86.6						
303	1	6.5	69.5	11.5	2.6	0.0		24.9	0.0	5.1	16.2	31.8							
304	10	6.9	71.0	14.5	15.4	7.1	21.9	45.8	0.0	10.6	32.0	52.6	91.7						
305	11	6.9	59.3	10.6	13.1	3.5	13.9	38.4	0.0	10.2	17.4	45.2	80.2						
306	10	6.9	67.2	11.6	14.0	3.9	15.3	42.5	0.0	11.9	20.9	50.2	88.1						
307	19	6.8	56.8	10.5	14.8	2.1	17.0	42.9	0.0	11.1	16.5	45.2	78.5						
308	4	6.8	59.9	9.8	15.1	0.0	21.2	34.2	0.0	10.6	30.7	54.5	95.5						
309	3	6.9	66.2	11.6	13.8	0.0	20.0	44.6	0.0	14.9	24.1	44.4	97.7						
310	40	6.6	72.3	11.8	15.1	4.1	20.3	42.6	0.0	9.7	25.7	49.6	88.2	0.0	0.0	0.0	0.0	3.6	0.0
311	32	6.5	64.7	12.1	14.4	5.3	17.3	43.2	0.0	11.1	21.6	41.4	85.9	0.0	0.0	0.0	0.0	3.4	0.0
312	3	6.9	58.3	10.6	12.7	2.8	18.5	33.9	0.0	7.8	21.1	51.7	80.4						
313	1	6.8	46.5	7.9	11.6	6.1	16.5	32.2	0.0	9.8	19.2	45.3	72.2						
315	4	6.7	66.9	10.4	11.3	1.9	18.2	32.6	0.0	12.3	21.4	42.7	77.1						
316	2	6.8	93.0	13.2	12.2	0.0	12.7	44.8	0.0	12.7	19.9	39.5	92.0						
317	2	6.7	84.6	13.2	10.7	0.0	15.4	43.7	0.0	14.0	22.9	38.1	92.6						
318	2	7.0	88.2	13.6	12.6	0.0	14.7	52.7	0.0	11.7	25.2	37.5	99.7						
319	10	6.9	77.3	11.8	13.4	0.0	17.4	46.5	0.0	12.3	26.6	43.1	98.4						
320	7	6.8	50.8	10.8	12.6	2.9	16.0	39.7	0.0	9.6	19.3	50.3	75.0						
321	8	7.1	95.1	14.1	13.7	0.0	16.4	60.6	0.0	21.2	27.3	63.7	133.9						
322	9	6.9	53.9	10.9	12.2	4.6	15.6	37.9	0.0	10.4	19.5	48.9	80.6						
323	4	6.9	62.9	11.1	11.7	2.8	18.4	37.2	0.0	10.9	24.6	52.6	94.0						
324	4	6.9	66.4	10.5	13.8	0.0	13.5	37.5	0.0	12.8	18.2	39.5	78.7						
325	4	6.8	67.4	11.1	11.0	0.0	17.2	41.0	0.0	12.3	26.2	53.7	109.4						
326	7	6.9	70.7	12.2	11.0	3.5	18.8	39.9	0.0	12.1	27.1	59.0	107.1						
327	15	7.0	82.0	14.7	17.2	11.8	23.1	49.9	0.0	13.4	21.4	67.2	109.6						
328	11	6.8	49.1	10.7	15.7	11.9	10.5	34.9	0.0	14.4	11.3	36.9	76.0						
329	9	6.9	68.4	12.4	13.3	4.0	18.4	39.1	0.0	12.5	29.1	59.1	99.6						
330	16	6.8	63.2	13.4	11.2	6.4	35.7	34.1	0.0	10.7	22.9	66.1	82.8						
331	4	7.1	89.4	17.9	17.6	15.5	33.5	45.7	1.8	16.7	25.7	76.9	92.1						
332	8	6.9	67.3	12.3	11.1	8.8	14.4	46.1	0.0	8.5	14.2	62.5	96.0						

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333	3	5.6	8.3	17.9	15.6	31.8	68.3	19.4	0.0	3.9	47.7	75.7	24.6						
334	6	6.4	16.3	11.7	12.1	24.1	31.2	27.4	0.0	9.2	14.6	48.4	40.1						
335	11	7.6	398.7	46.3	16.3	3.9	39.3	51.1	0.0	14.8	113.8	448.1	589.4						
336	32	6.4	47.8	11.5	15.6	25.3	8.5	39.2	0.0	11.8	20.9	35.4	61.7	0.1	0.0	0.1	0.0	2.7	0.1
337	34	6.2	39.5	12.0	15.5	26.2	15.7	38.8	0.0	10.1	21.4	36.0	56.1	0.1	0.0	0.0	0.0	2.8	0.1
338	2	5.9	27.2	12.9	13.1	35.6	34.4	34.2	0.0	8.3	24.1	43.2	25.8						
340	5	7.0	82.9	13.2	13.1	3.2	30.4	53.8	0.0	17.7	25.4	52.1	111.0						
341	7	7.2	137.8	29.3	15.4	2.7	105.3	50.0	0.0	11.8	119.7	134.4	182.9						
342	8	7.0	81.4	19.8	14.9	0.0	69.1	44.3	0.0	11.7	95.4	86.8	148.1						
343	1	6.9	58.0	11.0	14.1	4.0	13.2	39.9	0.0	11.7	14.6	50.1	85.1						
344	1	7.0	65.6	10.7	13.3	0.0	11.8	42.3	0.0	10.1	18.4	48.7	94.5						
345	1	6.0	10.2	13.9	11.8	35.4	47.4	23.9	0.0	9.0	23.5	48.2	9.9						
346	1	6.6	23.9	11.4	11.8	30.0	17.7	34.5	0.0	11.3	18.4	38.8	43.5						
347	1	7.2	160.9	19.1	15.8	2.9	17.9	56.7	0.0	10.6	31.0	76.6	138.4						
348	1	6.7	33.1	13.3	53.7	29.9	28.8	14.1	32.3	13.3	31.1	45.0	-8.9						
349	1	6.9	72.2	10.9	10.3	3.1	11.5	55.0	0.0	14.5	12.5	48.0	105.0						
350	4	6.8	43.8	11.7	14.9	19.7	10.6	37.4	0.0	9.6	22.0	55.0	81.5						
351	2		415.0	60.6	22.1	0.0	211.6	118.2	0.0	20.5	221.6	373.0	499.5						
352	4	7.7	440.6	64.7	20.0	1.3	133.0	106.1	0.0	14.6	166.4	384.9	504.7						
353	3	7.1	82.4	15.5	12.8	28.7	31.5	35.6	0.0	10.9	31.7	77.5	86.6						
354	4	6.8	56.3	14.0	15.2	24.1	13.4	40.7	0.0	11.3	18.8	56.2	89.6						
355	4	7.1	84.8	13.8	12.5	1.7	24.0	38.7	0.0	13.7	21.1	64.5	100.7						
356	1	5.4	-4.3	12.3	16.2	64.4	15.6	28.1	0.0	12.1	16.1	34.8	-5.1						
357	4	7.1	82.4	11.3	12.2	10.1	11.7	43.7	0.0	11.0	16.7	52.1	82.3						
360	5	4.6	-24.4	24.0	15.6	38.8	73.5	14.3	0.0	3.2	23.3	39.7	-45.3						
361	1	5.0	-8.9	26.3	11.6	89.3	72.1	25.5	5.0	8.6	33.6	90.0	-15.4						
362	2	6.9	57.8	10.7	14.4	5.6	15.0	31.9	0.0	9.8	18.6	54.6	79.9						
363	8	6.9	73.3	13.5	12.4	11.0	22.3	43.9	0.0	12.7	22.4	82.1	100.5						
364	3	7.0	87.8	18.0	11.5	8.6	43.4	40.6	0.0	12.7	50.8	88.6	117.5						
366	3	6.8	145.3	23.0	14.8	0.0	66.8	25.9	0.0	21.0	75.9	157.5	200.5						
367	1	6.9	96.3	14.3	9.1	1.7	15.0	66.9	0.0	11.7	17.8	55.4	126.1						
368	1	6.7	48.4	20.2	8.9	33.2	48.4	34.1	0.0	8.5	26.7	104.4	83.2						
369	2	5.8	18.5	15.5	13.6	30.5	55.4	28.5	0.8	8.0	23.0	60.7	20.8						

Site ID	N	pH	ANC	Cond	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BCS	Al	Cu	Fe	Mn	Si	Zn
377	1	7.6	270.4	33.6	14.9	2.2	39.9	83.1	0.0	7.9	93.0	228.5	355.4						
393	2	7.0	61.6	10.3	10.6	0.9	13.7	38.5	0.0	10.4	27.2	68.3	119.2						
399	1	6.7	49.5	7.9	17.0	4.0	9.9	36.1	0.0	8.0	15.4	48.6	77.2						
400	1	6.9	53.1	8.4	13.1	3.0	9.8	32.4	0.0	8.3	16.5	47.3	78.6						
401	1	6.7	42.0	7.8	14.0	2.7	10.3	29.4	0.0	6.1	16.0	43.1	67.7						
402	1	6.9	54.4	8.4	12.9	2.4	12.4	32.1	0.0	7.2	19.0	49.5	80.1						
472	20	6.2	29.8	12.0	15.5	14.0	32.9	34.1	0.0	8.2	20.7	42.1	43.9	0.0	0.0	0.0	0.0	2.2	0.0
473	24	6.3	38.3	21.0	18.7	31.4	82.1	24.4	0.0	5.4	50.2	105.4	43.6	0.0	0.0	0.0	0.0	1.7	0.0
474	23	6.4	53.0	13.2	14.1	12.6	31.6	37.8	0.0	10.0	22.1	53.4	60.7	0.1	0.1	0.0	0.0	2.8	0.1
475	20	6.4	39.1	12.0	16.5	15.3	27.0	36.4	0.0	10.6	20.3	41.8	46.2	0.1	0.0	0.0	0.0	2.5	0.0
479	28	6.5	70.4	11.8	14.2	3.6	17.3	43.6	0.0	11.8	21.9	42.2	87.2	0.0	0.0	0.0	0.0	3.4	0.0
480	30	6.6	90.3	13.4	13.0	2.1	21.6	48.6	0.0	12.2	29.7	48.2	100.4	0.0	0.0	0.0	0.0	4.2	0.0
481	27	6.6	92.5	16.9	12.9	0.0	55.6	45.1	0.0	13.0	51.9	56.9	90.2	0.0	0.0	0.0	0.0	4.3	0.2
482	26	6.5	85.8	13.9	14.7	2.4	20.6	47.0	0.0	11.3	35.5	48.2	102.4	0.0	0.0	0.0	0.0	4.3	0.0
483	29	6.6	88.7	14.4	13.9	1.7	30.2	48.6	0.0	13.6	35.8	51.2	103.1	0.0	0.0	0.0	0.0	4.3	0.0
484	27	6.5	53.7	10.5	14.6	7.6	16.3	38.0	0.0	10.6	18.5	36.7	72.9	0.0	0.0	0.0	0.0	3.3	0.0
485	26	6.5	70.8	11.1	13.7	2.9	14.7	40.3	0.0	11.1	22.2	42.6	89.4	0.0	0.0	0.0	0.0	3.7	0.0
487	3	7.0	83.9	16.2	16.0	0.0	44.7	51.1	0.0	13.2	44.7	80.2	127.8						
488	51	6.4	46.8	11.8	15.4	11.3	22.7	39.6	0.0	9.7	20.7	40.4	60.1	0.0	0.0	0.0	0.0	2.7	0.0
489	46	7.6	944.3	96.0	19.3	11.0	47.4	53.9	0.0	14.8	179.5	787.1	971.1	0.0	0.0	0.0	0.0	3.4	0.0
490	3	7.0	67.3	12.2	13.7	0.0	32.6	33.9	0.0	11.1	26.3	76.3	119.3						
492	63	6.3	28.2	16.7	13.3	41.8	46.2	32.8	0.0	8.8	34.3	63.0	36.7	0.0	0.0	0.0	0.0	2.3	0.0
493	54	6.6	65.1	12.2	12.3	9.3	18.3	41.5	0.0	12.0	19.0	41.4	73.4	0.0	0.0	0.0	0.0	2.9	0.0
494	1	7.1	92.7	15.5	11.5	0.0	21.8	48.9	0.0	16.8	50.5	92.3	175.3						

Table 7.2 Median stream chemistry for stormwater. Ion units: $\mu\text{eq L}^{-1}$ except pH as standard pH units, conductivity as $\mu\text{S cm}^{-1}$, and metals as mg L^{-1} .

Site ID	N	pH	ANC	Cond	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BCS	Al	Cu	Fe	Mn	Si	Zn
1	7	6.2	38.4	15.6	16.4	23.9	45.6	38.6	0.0	11.8	19.0	65.1	57.1	0.0	0.0	0.0	0.0	2.5	0.0
3	10	6.5	63.2	16.6	14.7	17.8	37.2	44.9	0.0	9.9	33.2	82.0	95.9	0.1	0.0	0.1	0.0	1.8	0.0
4	22	5.9	13.5	14.0	11.9	27.6	44.0	30.6	0.0	11.7	24.1	56.9	35.1	0.1	0.0	0.0	0.0	2.1	0.0
5	7	6.8	60.3	16.9	12.2	32.5	42.5	39.7	0.0	8.9	41.6	87.3	88.8						
6	2	6.9	66.3	15.3	10.3	12.6	39.7	36.2	0.0	10.6	38.5	56.0	78.7						
8	1		80.4	18.2	17.2	0.0	64.8	68.3	0.0	18.2	52.3	90.5	147.3						
9	1		162.1	27.4	18.4	3.9	80.1	77.8	0.0	41.3	81.5	144.3	242.4						
11	1		189.5	33.7	18.5	0.0	133.3	66.2	0.0	31.5	135.5	185.7	267.1						
12	1		51.6	10.0	11.2	0.0	26.1	40.9	0.0	11.5	31.1	58.9	105.1						
13	24	6.6	96.0	17.5	14.4	11.8	35.9	39.3	0.0	12.7	35.9	78.8	105.6	0.0	0.0	0.0	0.0	2.6	0.0
14	16	6.5	91.8	16.7	13.3	7.4	36.3	33.2	0.0	12.1	33.5	85.1	97.4						
15	1	6.9	56.8	14.9	13.4	0.0	56.9	48.8	0.0	10.5	47.9	61.5	98.4						
16	1	6.8	56.7	13.5	11.9	17.0	38.1	32.2	0.0	13.3	30.9	88.9	98.4						
17	1	6.8	48.9	13.2	11.4	16.8	36.9	30.4	0.0	10.0	27.4	82.9	85.5						
19	1	6.9	48.0	13.6	13.1	16.6	36.7	31.1	4.7	11.8	28.7	87.5	92.7						
20	15	6.5	82.2	14.2	12.5	7.6	34.4	36.8	0.0	11.2	28.6	82.6	84.7						
21	2	7.1	113.6	16.4	13.4	0.0	41.0	60.0	0.0	7.6	54.1	91.6	158.8						
22	3	7.3	148.4	20.7	15.5	0.0	20.9	73.3	0.0	4.7	82.5	87.0	218.3						
23	26	6.5	82.1	16.0	12.9	11.4	32.2	33.5	0.0	12.0	36.9	64.6	87.2	0.0	0.0	0.0	0.0	2.4	0.0
24	22	6.6	125.0	21.1	14.9	6.6	45.2	51.2	0.0	13.2	45.1	92.7	135.2	0.0	0.0	0.0	0.0	3.2	0.0
25	6	7.4	256.2	31.7	14.6	0.8	66.6	67.3	0.0	12.2	85.8	167.8	271.1						
26	1		106.8	18.8	15.7	5.2	46.4	59.3	0.0	13.1	36.9	115.8	157.8						
27	1	7.3	157.8	18.5	14.0	1.2	21.0	72.9	0.0	11.5	37.7	129.1	215.0						
28	1		47.3	15.3	13.4	11.5	58.8	36.2	0.0	11.7	30.3	96.5	91.0						
29	5	6.9	71.7	17.7	16.7	26.4	68.9	39.8	0.0	10.4	55.3	125.1	101.0						
30	24	6.3	42.8	20.4	15.4	31.5	67.0	31.7	0.0	9.0	45.5	99.4	65.0	0.0	0.0	0.0	0.0	2.1	0.0
31	1	6.4	16.7	17.9	15.2	42.0	70.6	22.1	0.0	7.4	44.1	105.7	51.5						
32	1	6.9	31.9	21.0	16.0	56.7	53.0	38.3	0.0	15.2	32.8	123.1	83.6						
34	13	6.4	44.0	13.4	20.1	13.5	34.4	29.9	0.0	10.9	24.2	63.1	65.1	0.1	0.0	0.0	0.0	2.7	0.0
35	4	6.9	55.1	13.2	12.3	14.3	33.7	30.9	0.0	11.4	28.4	78.6	79.3						
36	3	6.6	36.1	9.7	17.1	0.0	37.6	36.5	0.0	20.1	22.3	49.3	67.8						

Site ID	N	pH	ANC	Cond	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BCS	Al	Cu	Fe	Mn	Si	Zn
37	1	7.0	90.3	15.7	14.8	1.8	41.2	62.1	0.0	13.4	32.8	81.7	132.2						
40	4	6.5	42.2	11.3	11.1	17.2	34.2	28.4	0.0	10.4	24.0	76.3	62.1						
42	3	6.6	41.5	12.6	12.0	17.8	35.2	29.9	0.0	9.9	26.8	75.4	61.4						
43	16	5.7	5.3	16.4	13.5	28.4	74.2	23.1	0.0	5.5	38.9	57.7	6.0	0.1	0.0	0.0	0.0	1.9	0.0
44	2	6.0	8.4	13.5	20.8	46.6	134.4	17.9	0.0	8.1	22.0	130.1	-23.8						
45	11	5.4	-0.1	20.4	14.2	32.4	100.1	19.6	0.0	4.6	52.9	79.6	7.7	0.1	0.0	0.0	0.0	1.5	0.0
46	13	5.4	0.5	18.8	13.6	31.7	86.9	23.6	0.0	3.8	49.6	68.3	-1.1	0.2	0.0	0.0	0.0	1.8	0.1
47	11	5.8	9.2	12.4	11.7	22.5	43.9	23.4	0.0	8.5	21.9	45.0	23.4	0.1	0.0	0.0	0.0	2.2	0.0
48	3	6.4	17.9	17.1	11.2	26.5	69.2	26.9	0.0	6.2	37.2	68.6	31.4						
49	10	6.1	19.9	16.2	14.1	21.9	60.1	29.1	0.0	7.5	36.0	69.5	48.4	0.0	0.0	0.0	0.0	2.0	0.0
50	11	6.2	17.3	15.3	14.8	22.7	49.0	32.8	0.0	8.6	32.1	72.8	41.5	0.1	0.0	0.0	0.0	2.3	0.0
51	2	6.7	52.6	16.3	11.0	14.6	51.8	36.6	0.0	11.3	32.6	78.2	81.4						
52	13	6.3	32.8	16.0	14.6	22.0	52.1	32.5	0.0	8.2	30.3	65.6	41.6	0.0	0.0	0.0	0.0	2.5	0.0
53	1	5.1	-5.8	16.3	26.7	31.6	84.4	18.6	0.0	45.9	21.1	65.2	8.2						
54	1	6.2	23.0	12.2	12.4	23.9	74.0	24.1	0.0	28.7	31.3	89.7	63.4						
55	1	6.4	38.6	11.5	15.1	26.7	50.3	30.3	0.0	21.0	25.8	84.8	69.8						
56	2	6.6	39.3	17.4	21.0	21.1	62.6	32.9	0.0	22.9	27.6	96.7	75.3						
59	1	--	20.1	14.9	13.5	19.1	65.0	27.7	0.0	11.8	26.3	82.0	50.2						
60	2	--	0.3	17.0	15.8	23.4	90.3	25.0	0.0	12.1	28.5	81.7	17.8						
61	1	--	-5.9	19.2	13.1	23.7	93.4	21.5	0.0	11.5	29.2	74.9	7.0						
62	1	--	-7.2	20.3	13.2	22.5	98.9	21.3	0.0	10.2	30.0	67.2	-5.8						
63	1	--	-5.2	18.3	19.1	22.2	89.4	24.6	0.0	15.7	30.2	77.3	17.0						
64	1	--	11.8	15.2	13.5	21.2	71.4	28.3	0.0	11.5	27.0	87.1	47.9						
66	29	6.1	28.9	19.4	15.0	35.9	69.1	22.2	0.0	6.5	44.0	102.4	43.9	0.1	0.0	0.0	0.0	1.7	0.0
67	1	6.3	15.9	23.6	13.0	45.8	121.7	19.6	0.0	8.1	67.7	138.7	53.6						
68	1	5.7	8.8	17.0	15.4	42.7	70.0	19.1	0.0	6.3	42.1	92.3	31.7						
69	5	5.6	1.3	18.7	17.5	48.4	59.1	23.4	0.0	6.1	55.1	69.0	32.5						
70	2	6.1	14.2	15.0	12.1	36.6	61.6	23.7	0.0	8.8	22.7	86.8	39.6						
71	24	6.0	19.9	15.8	12.4	36.9	48.4	24.1	0.0	8.8	28.2	73.4	38.7	0.1	0.0	0.0	0.0	1.9	0.0
72	6	6.4	25.8	15.4	11.6	35.4	52.3	26.2	0.0	8.7	31.0	88.1	48.0						
73	23	6.1	30.2	20.5	16.0	37.3	77.5	21.9	0.0	5.2	48.9	100.7	44.1	0.1	0.0	0.0	0.0	1.5	0.0
74	22	6.4	39.0	23.6	16.6	39.2	83.6	24.8	0.0	5.7	48.5	122.1	57.0	0.1	0.0	0.0	0.0	1.5	0.0
75	7	5.1	-6.8	18.8	11.6	30.7	72.9	15.1	0.0	3.6	43.5	47.4	-15.2						

Site ID	N	pH	ANC	Cond	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BCS	Al	Cu	Fe	Mn	Si	Zn
76	6	5.0	-10.1	18.0	12.4	31.9	70.4	15.6	0.0	2.8	41.4	48.5	-16.3						
77	1		13.8		10.6	29.1	39.2	16.3	0.0	3.1	39.0	26.1	5.5						
79	5	4.7	-23.2	24.2	16.1	28.4	83.9	14.3	0.0	4.2	32.4	43.9	-36.8						
80	2	5.3	-5.1	18.2	10.6	38.0	68.4	19.4	0.0	2.8	35.0	67.1	7.3						
82	3	6.4	21.0	15.3	11.7	19.8	39.5	21.7	0.0	3.4	19.8	45.2	33.9						
83	2	6.4	38.0	15.0	22.3	46.0	87.1	30.0	0.0	12.9	39.5	150.6	77.6						
84	3	6.2	14.4	14.3	11.2	26.1	44.4	35.3	0.0	9.0	27.9	59.7	44.8						
86	2	6.2	13.9	14.3	12.5	32.1	48.0	35.4	0.0	10.6	25.4	68.2	47.1						
87	4	6.2	15.6	14.9	15.7	33.7	51.2	32.4	0.0	10.6	28.0	66.4	39.4						
88	2	6.1	14.1	14.1	13.4	29.0	44.9	37.0	0.0	9.9	22.6	63.9	46.1						
90	1	5.8	8.6	8.4	10.9	9.9	49.9	40.5	0.0		105.3	287.7							
91	2	6.4	24.5	13.3	17.2	22.1	38.2	39.4	1.8	11.5	21.4	59.3	54.1						
92	3	4.9	-10.4	17.6	16.5	12.5	56.9	33.0	0.0	9.3	11.4	35.5	0.1						
93	5	5.5	0.5	17.1	21.4	34.3	44.9	29.9	0.0	12.4	18.1	48.9	23.6						
94	1	5.6	3.0	14.3	18.1	21.0	44.0	23.7	0.0	20.6	17.1	47.1	25.4						
95	1	5.5	2.8	15.8	11.7	20.0	47.3	27.0	0.0	23.6	18.1	41.2	31.0						
99	1	6.2	24.1	10.2	10.7	20.7	22.9	22.5	0.0	10.2	20.9	62.7	62.1						
100	1	6.9	77.2	12.5	13.9	9.1	24.6	46.1	0.0	14.0	28.3	67.5	108.4						
103	7	5.4	2.0	21.8	17.4	60.2	66.2	30.1	0.0	13.7	24.3	89.7	25.1	0.1	0.0	0.0	0.0	1.4	0.0
104	7	5.6	4.0	18.2	13.9	51.7	55.0	26.5	0.0	12.3	20.6	70.0	19.7	0.1	0.0	0.0	0.0	1.3	0.1
105	3	6.5	15.6	16.8	13.1	33.3	59.6	30.3	0.0	11.8	26.3	92.0	50.8						
106	6	5.9	10.8	18.3	16.7	47.4	56.6	26.5	0.0	14.4	23.1	94.2	44.4	0.1	0.0	0.0	0.0	1.3	0.0
107	8	5.9	15.8	16.6	13.4	40.4	52.0	26.7	0.0	13.3	21.9	84.2	55.7	0.1	0.0	0.0	0.0	1.3	0.0
110	6	5.6	0.1	16.5	16.6	63.1	20.1	33.2	0.0	6.0	22.3	45.0	8.6						
111	5	6.6	43.6	12.0	11.4	21.6	19.4	33.4	0.0	6.5	22.2	53.9	60.5						
112	5	4.4	-38.7	28.3	10.8	38.4	76.9	29.0	0.0	7.4	17.8	33.7	-36.8						
113	5	4.4	-39.5	25.0	9.5	31.6	72.6	29.1	0.0	9.5	7.2	45.9	-39.9						
114	20	6.3	38.7	17.9	13.2	41.0	49.0	34.3	0.0	11.2	36.2	68.5	47.6	0.0	0.0	0.0	0.0	2.2	0.0
115	6	6.2	40.6	18.5	18.1	37.2	52.0	35.5	0.0	8.2	36.7	76.9	49.4	0.0	0.0	0.0	0.0	1.5	0.0
125	3	7.0	84.4	12.3	10.9	4.1	11.7	57.1	0.0	14.1	21.7	71.1	136.2						
126	1	6.7	40.2	14.7	16.1	34.6	7.1	37.9	0.0	23.7	13.9	53.4	71.1						
127	6	6.3	38.2	11.1	16.3	15.3	20.9	35.4	0.0	11.2	18.7	47.6	52.5						
128	2	6.9	78.1	18.6	15.1	1.6	14.3	49.8	0.0	17.2	25.9	63.5	125.4						

Site ID	N	pH	ANC	Cond	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BCS	Al	Cu	Fe	Mn	Si	Zn
129	2	6.8	55.8	14.7	14.8	9.9	15.8	45.8	0.0	12.4	23.7	61.5	102.8						
130	1	6.7	42.3	12.3	11.7	22.1	19.8	41.7	0.0	10.6	19.9	54.2	72.7						
131	2	6.8	52.8	8.6	13.7	23.3	34.0	41.0	0.0	12.6	31.8	84.2	98.7						
132	4	6.4	33.5	11.1	11.8	14.7	29.7	31.1	0.0	9.3	24.7	65.5	71.2						
133	4	6.4	30.6	13.5	12.7	21.0	38.5	32.2	0.0	8.8	32.9	72.1	73.5						
134	6	6.8	82.0	17.2	10.7	19.4	46.8	35.7	0.0	7.8	54.3	99.0	126.8						
135	3	6.5	35.0	12.6	11.5	21.9	46.4	32.6	0.0	7.6	39.7	80.9	87.7						
137	22	5.8	9.4	15.8	12.6	36.4	52.5	29.7	0.0	9.8	27.3	56.9	22.8	0.0	0.0	0.0	0.0	2.1	0.0
138	9	5.5	4.5	13.8	14.6	34.5	36.7	26.8	0.0	8.8	18.5	48.8	16.1	0.1	0.0	0.0	0.0	1.3	0.2
140	4	6.8	43.7	9.5	10.9	9.8	18.8	24.3	0.0	7.3	15.9	39.4	48.9						
141	3	6.9	66.6	10.8	11.8	2.8	14.4	34.4	0.0	11.7	19.1	58.6	94.9						
142	14	6.4	57.3	11.7	12.9	7.9	17.8	36.6	0.0	12.8	17.0	40.5	70.9	0.0	0.0	0.0	0.0	3.0	0.0
143	14	6.4	52.4	10.8	16.9	7.0	21.9	34.7	0.0	12.5	17.1	36.9	60.7	0.0	0.0	0.0	0.0	2.8	0.0
144	13	6.4	64.5	11.7	15.2	7.9	20.5	36.5	0.0	12.8	18.5	45.8	66.3	0.0	0.0	0.0	0.0	3.1	0.0
145	1	7.0	78.2	13.7	13.2	2.6	22.4	43.0	0.0	16.6	33.8	64.9	120.0						
146	3	7.0	66.5	11.7	12.3	7.3	18.8	35.2	0.0	10.7	21.1	60.9	89.6						
147	18	6.6	86.4	14.8	15.4	11.3	23.2	45.4	0.0	15.2	25.3	54.3	87.9	0.0	0.0	0.0	0.0	3.8	0.0
148	11	6.7	113.8	17.1	12.6	3.6	23.0	60.8	0.0	18.5	30.1	69.5	130.5	0.0	0.0	0.0	0.0	4.4	0.0
149	12	6.5	75.8	15.1	15.8	9.5	23.3	49.3	0.0	17.8	26.1	56.8	106.9	0.0	0.0	0.0	0.0	3.7	0.0
150	6	6.4	65.4	12.9	16.7	9.4	22.7	43.2	0.0	12.8	25.9	62.2	95.9						
151	4	7.0	86.5	22.4	16.0	0.0	70.3	45.6	0.0	18.4	63.1	72.8	123.4						
152	6	7.7	413.5	45.7	17.6	7.3	39.0	48.8	0.0	13.8	85.8	344.2	415.6						
153	4	7.6	329.6	38.4	16.0	5.1	43.0	46.0	0.0	13.9	77.2	288.1	352.1						
156	12	7.1	270.0	37.2	19.9	4.2	40.3	46.7	0.0	15.1	72.1	249.9	294.0						
163	1		271.0	56.3	16.7	0.0	294.2	83.8	0.0	35.2	253.5	295.4	356.9						
164	1		136.1	24.0	18.3	0.0	83.0	60.8	0.0	27.8	104.3	125.8	217.5						
165	1		280.7	33.7	15.2	0.0	55.5	53.2	0.0	55.4	124.9	209.5	372.3						
166	1		128.9	26.5	19.4	1.5	95.9	82.1	0.0	41.5	77.3	117.2	201.3						
167	1		96.6	17.9	20.5	0.0	47.1	53.1	0.0	37.6	51.5	89.0	163.7						
168	2	7.0	97.5	21.3	14.2	0.0	68.6	60.4	0.0	15.0	69.5	75.3	137.5						
169	4	7.1	109.9	22.3	16.2	0.0	71.2	71.8	0.0	14.1	69.3	84.3	151.3						
170	2	6.9	73.7	18.6	13.9	2.0	64.0	51.4	0.0	16.2	60.8	72.2	120.6						
171	2	7.6	330.2	45.7	26.7	5.4	101.9	64.6	3.0	19.2	147.1	312.1	409.2						

Site ID	N	pH	ANC	Cond	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BCS	Al	Cu	Fe	Mn	Si	Zn
173	23	6.7	78.7	16.9	15.9	9.3	28.6	38.4	0.0	13.2	38.4	63.0	94.3	0.0	0.0	0.0	0.0	2.8	0.0
174	22	7.3	706.4	78.8	19.3	12.6	47.3	49.7	0.0	15.9	138.0	559.7	733.0	0.0	0.0	0.0	0.0	3.3	0.0
175	4	7.0	65.2	16.7	14.1	0.0	56.0	41.2	0.0	19.7	45.8	78.2	112.3						
176	4	7.6	356.9	42.8	16.4	6.9	49.4	48.2	0.0	14.9	84.4	324.1	391.6						
177	1	6.8	41.1	9.5	12.1	3.2	22.9	34.4	0.0	12.7	22.1	72.0	102.9						
183	7	5.6	38.4	8.4	18.8	5.9	7.3	28.1	0.0	9.1	11.0	21.7	40.8						
184	7	6.1	25.8	12.5	21.1	28.8	30.7	30.8	0.0	11.0	18.7	54.1	38.9						
185	5	6.6	36.0	11.5	14.8	22.5	28.2	41.0	0.0	10.9	21.8	62.3	67.8						
186	14	6.2	37.3	13.6	17.9	19.1	30.1	35.8	0.0	11.4	23.6	67.9	56.8						
190	10	6.1	20.9	11.6	13.9	18.7	33.2	27.5	0.0	7.9	18.6	42.6	40.5	0.1	0.0	0.0	0.0	2.6	0.0
191	10	6.1	19.7	10.4	17.0	19.3	27.4	23.8	0.0	8.7	15.1	39.2	22.9	0.2	0.0	0.0	0.0	2.1	0.0
192	12	6.0	16.4	12.7	13.3	24.4	44.9	22.3	0.0	6.0	23.5	53.2	17.9	0.0	0.0	0.0	0.0	2.2	0.0
193	16	6.3	40.6	10.6	15.2	8.3	26.7	28.7	0.0	9.2	20.4	45.4	58.2	0.1	0.0	0.0	0.0	2.6	0.0
194	13	6.3	34.5	11.4	16.6	12.1	29.6	28.5	0.0	8.3	22.8	48.2	43.1	0.1	0.0	0.0	0.0	2.6	0.0
195	4	5.7	27.7	7.8	15.4	3.5	7.9	24.4	0.0	6.3	9.6	16.4	28.6						
199	2	7.1	102.6	14.3	14.8	4.0	23.2	33.2	0.0	12.7	27.7	82.8	114.4						
200	8	6.0	19.9	13.1	16.8	30.7	27.7	29.4	0.0	11.9	17.5	55.9	28.4						
201	6	5.5	33.7	10.8	12.4	14.2	15.0	24.0	0.0	9.4	12.8	31.7	34.0						
207	2		41.2	8.5	11.1	5.4	13.4	33.8	0.0	8.8	17.8	50.4	81.0						
209	14	6.1	31.7	9.4	15.9	4.0	24.6	33.7	0.0	10.0	16.1	26.8	42.9	0.2	0.0	0.0	0.0	3.1	0.0
210	14	6.3	43.7	13.8	18.0	15.6	39.7	29.8	0.0	10.0	21.7	56.9	45.2	0.1	0.0	0.0	0.0	2.6	0.0
211	1	6.5	36.4	12.0	26.6	26.4	66.8	28.2	0.0	10.8	26.9	69.0	15.1						
212	3	6.3	28.9	10.7	23.3	25.6	38.5	30.0	0.0	12.6	25.4	68.2	48.8						
213	15	5.9	19.7	11.2	15.3	24.8	30.3	24.2	0.0	8.7	19.4	34.7	31.9	0.1	0.0	0.0	0.0	2.3	0.0
214	15	6.2	33.8	10.5	16.0	17.3	23.7	32.4	0.0	10.1	18.1	35.0	41.2	0.1	0.0	0.1	0.0	2.6	0.0
215	15	6.3	47.7	12.4	17.6	12.0	34.0	34.4	0.0	10.0	25.5	50.4	60.0	0.1	0.0	0.0	0.0	3.1	0.0
218	13	5.0	2.0	22.2	17.1	48.1	54.6	25.4	0.0	13.2	20.3	42.0	-20.8						
219	9	4.9	-0.6	25.1	14.8	87.2	53.9	21.5	0.0	11.6	20.1	40.2	-72.0						
220	8	5.3	-0.9	16.7	12.0	69.2	27.6	25.6	0.0	11.2	20.8	51.3	-4.0						
221	8	6.1	25.5	10.4	13.7	29.4	18.3	31.2	0.0	8.9	18.6	39.4	32.6	0.0	0.0	0.0	0.1	2.3	0.0
223	1	6.9	62.3	11.1	15.5	0.0	19.9	38.2	0.0	14.0	27.5	73.9	118.1						
224	5	6.2	35.9	11.3	12.2	13.2	17.7	32.6	0.1	11.9	18.7	33.2	52.8	0.0	0.0	0.0	0.0	2.3	0.0
225	2	5.9	8.9	12.7	11.4	24.0	47.2	25.9	0.0	8.5	14.4	56.8	22.9						

Site ID	N	pH	ANC	Cond	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BCS	Al	Cu	Fe	Mn	Si	Zn
226	2	5.9	11.6	10.9	8.2	19.3	39.1	23.3	0.0	6.9	13.5	47.9	25.0						
227	1	6.1	11.8	14.1	9.1	23.7	50.0	24.8	0.0	6.0	12.5	61.0	21.6						
228	6	6.3	21.2	10.3	12.4	18.4	32.4	28.9	0.0	9.3	18.2	56.7	41.4						
229	3	6.5	34.9	9.8	11.8	6.9	26.3	31.0	0.0	9.0	18.3	53.2	51.4						
230	3	6.4	23.0	10.1	13.1	12.5	29.1	33.5	0.0	8.9	17.6	54.8	42.1						
231	3	6.5	41.5	10.1	11.0	12.2	23.0	31.6	0.0	9.8	18.4	55.5	53.5						
232	1	5.1	-8.0	18.4	12.4	54.0	66.9	17.6	0.0	5.3	32.2	75.9	-2.5						
233	24	5.8	12.4	23.9	16.5	43.8	97.3	22.7	0.0	5.0	52.2	99.9	25.0	0.1	0.0	0.0	0.0	1.3	0.0
234	19	5.9	15.1	15.7	13.9	57.6	28.2	31.9	0.0	7.2	28.9	54.7	22.5	0.0	0.0	0.0	0.0	2.2	0.0
235	1	6.2	13.6	15.0	12.6	44.8	46.2	20.1	0.0	19.3	25.9	74.0	35.7						
236	7	5.5	-2.2	17.7	11.4	42.4	77.0	18.4	0.0	4.3	39.5	59.8	-11.0						
237	32	4.7	-16.9	21.2	12.6	40.5	68.3	15.9	0.0	3.7	31.7	51.1	-23.5	0.2	0.0	0.0	0.0	1.3	0.0
242	2	5.2	-1.6	19.3	13.1	41.5	42.3	25.3	0.9	8.6	18.7	33.8	-10.5						
243	7	5.5	-0.9	15.0	9.6	36.1	58.7	16.0	0.0	8.8	20.9	59.8	1.0						
244	6	6.2	9.8	12.7	11.0	36.6	36.6	27.0	0.0	7.7	20.5	58.8	34.0						
245	2	6.7	38.7	7.0	9.6	0.0	5.8	30.5	0.0	8.8	12.1	27.7	47.1						
246	5	6.4	18.4	11.4	11.2	36.3	30.7	27.8	0.0	9.2	20.5	54.3	31.5						
247	4	6.5	24.8	11.0	12.3	18.3	26.3	27.5	0.0	9.2	19.2	44.3	48.7						
248	6	6.6	30.4	10.6	10.8	14.5	25.0	29.2	0.0	8.9	18.5	44.6	52.3						
250	1	6.7	34.9	10.0	10.3	11.1	32.1	24.5	0.0	9.3	17.2	60.8	58.3						
251	21	6.1	22.9	31.4	15.8	39.7	163.0	38.6	0.0	11.2	79.3	124.2	41.1	0.0	0.0	0.0	0.0	2.6	0.0
252	19	4.9	-5.7	54.6	15.4	51.2	361.5	45.1	0.0	16.3	148.5	156.1	-62.5	0.4	0.0	0.0	0.4	3.4	0.0
253	19	6.4	91.8	24.0	15.1	56.3	43.6	51.8	0.0	9.9	51.6	108.5	100.4	0.0	0.0	0.0	0.0	3.2	0.0
254	4	7.0	61.1	14.5	13.9	37.3	41.3	39.3	0.0	10.9	28.4	65.4	67.2						
255	1	6.8	49.0	13.1	12.1	42.2	12.3	31.7	0.0	9.8	24.5	51.6	51.0						
256	1	6.8	44.6	12.3	10.9	27.8	23.7	29.3	0.0	8.8	23.4	48.0	47.0						
257	2	6.7	53.7	11.6	13.9	17.5	21.7	35.9	0.0	12.1	25.4	62.6	82.8						
258	2	6.8	46.8	9.9	10.0	10.1	19.6	26.7	0.0	9.7	20.0	38.6	55.2						
259	1	6.4	43.5	9.1	9.9	10.7	20.4	33.6	0.0	11.2	21.4	42.2	67.4						
260	4	6.8	58.7	10.9	12.1	0.0	26.9	37.5	0.0	15.7	30.7	74.3	117.4						
261	3	6.7	56.2	10.8	12.7	0.0	27.9	37.9	0.0	14.8	24.2	49.2	87.0						
262	2	6.5	50.5	10.2	10.8	1.0	23.4	33.6	0.0	13.2	21.8	52.0	85.4						
263	4	6.5	43.6	10.2	10.2	0.0	33.5	30.1	0.0	13.8	23.7	54.4	78.8						

Site ID	N	pH	ANC	Cond	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BCS	Al	Cu	Fe	Mn	Si	Zn
264	3	6.6	34.9	10.3	10.4	0.0	23.6	31.7	0.0	12.5	22.5	53.9	79.1						
265	2	7.0	73.0	10.7	15.4	0.0	9.1	43.7	3.9	15.7	25.0	61.1	121.0						
266	4	6.3	52.5	12.7	17.0	11.3	27.1	40.8	0.0	10.9	24.1	65.5	90.2						
267	5	6.7	53.1	13.3	13.6	21.2	31.1	34.1	0.0	11.7	22.5	67.3	67.8						
268	21	6.3	46.5	13.7	12.1	17.1	36.1	34.9	0.0	10.5	28.2	54.4	64.2	0.0	0.0	0.0	0.0	2.6	0.0
269	1	6.7	41.3	10.7	10.7	12.5	30.0	29.5	1.6	9.4	25.0	62.3	73.1						
270	12	6.4	48.6	12.5	9.7	15.4	31.1	32.1	0.0	10.0	22.4	48.0	54.2	0.0	0.0	0.0	0.0	2.2	0.0
271	7	7.0	85.7	12.9	9.4	5.1	15.8	51.9	0.0	11.1	21.7	63.5	108.6						
272	1	6.4	21.5	14.4	17.3	24.8	57.7	27.1	1.9	6.7	37.9	70.0	42.0						
273	2	6.7	49.8	13.3	12.8	12.9	35.7	39.6	1.7	9.1	29.3	61.8	78.4						
274	1	6.7	58.1	8.1	9.3	2.9	9.4	29.1	0.0	8.1	14.3	35.1	64.9						
275	1	6.8	73.3	10.2	9.2	2.4	12.7	38.2	0.0	9.6	24.2	44.8	92.6						
276	2	6.4	36.6	11.0	15.7	21.8	16.7	35.9	0.0	14.6	21.8	61.8	80.0						
277	4	6.2	27.9	11.1	13.6	26.1	24.2	35.6	0.0	11.1	20.9	56.1	59.2						
278	6	6.9	62.3	10.4	11.8	7.1	10.3	34.1	0.0	9.0	17.9	45.7	86.6						
279	8	6.9	64.0	10.1	9.7	3.9	8.8	38.5	0.0	9.3	14.7	47.9	90.4						
280	5	6.5	19.2	13.4	11.1	21.8	48.9	28.6	0.0	7.2	35.1	68.9	55.8						
281	4	6.7	34.3	14.1	10.2	20.8	49.2	30.7	0.0	7.0	34.6	70.0	63.1						
282	7	6.8	43.2	13.1	11.2	18.8	40.0	34.6	0.0	9.3	31.2	66.8	76.8						
283	6	6.8	49.8	15.0	10.8	14.8	46.3	39.3	0.0	9.0	31.5	68.1	78.7						
284	1	7.0	64.1	14.6	12.1	10.1	31.6	46.3	0.0	11.9	41.5	97.4	143.4						
285	1	7.1	134.1	17.4	13.8	0.0	14.6	76.2	0.0	18.7	33.0	92.4	192.0						
286	1	6.8	72.8	15.7	15.0	27.3	24.0	46.9	0.0	12.7	36.2	78.7	108.1						
287	1	6.9	77.4	15.9	14.3	20.1	24.6	45.5	0.0	13.3	35.0	79.0	113.8						
288	1		77.1	13.2	18.1	20.2	15.9	51.1	0.0	17.7	21.6	79.8	116.0						
289	1	6.6	46.4	14.6	11.6	24.6	33.1	44.5	0.0	12.6	20.5	72.1	80.4						
290	11	4.9	-3.3	16.2	16.9	46.6	26.2	31.5	0.0	8.7	24.8	46.6	8.8						
291	10	6.0	21.6	13.5	15.3	35.9	25.7	32.9	0.0	11.2	26.1	64.5	45.3						
292	2	6.7	63.6	11.8	12.2	10.9	24.2	44.7	0.0	16.2	23.9	80.6	118.1						
293	15	6.7	83.4	16.8	14.1	17.5	25.2	47.9	0.0	14.5	29.1	62.6	97.3	0.0	0.0	0.0	0.0	3.7	0.0
294	2	6.9	61.3	13.1	15.0	10.9	18.7	40.0	0.0	11.9	31.0	61.6	99.9						
295	1	6.9	80.0	14.5	18.1	6.4	20.7	45.7	0.0	17.5	33.5	71.3	122.8						
299	3	6.9	68.3	12.5	14.5	0.0	16.2	50.0	0.0	14.8	19.2	40.6	94.5						

Site ID	N	pH	ANC	Cond	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BCS	Al	Cu	Fe	Mn	Si	Zn
304	3	6.7	62.8	14.3	17.9	18.8	36.0	51.2	0.0	14.5	33.0	59.7	89.4						
305	3	6.9	56.9	9.3	13.1	1.9	14.2	42.5	0.0	10.6	17.7	38.2	83.0						
306	2	7.0	71.6	11.8	17.3	1.1	14.2	47.4	0.8	16.0	19.7	42.2	92.5						
307	6	6.8	52.1	8.9	14.7	0.0	17.1	41.5	0.0	11.2	15.5	32.6	69.2						
309	1	6.8	53.0	12.0	13.8	0.0	28.9	42.1	0.0	20.2	22.6	32.5	74.7						
310	12	6.4	66.8	13.1	12.5	5.4	21.5	37.2	0.0	10.6	25.6	49.9	79.8	0.0	0.0	0.0	0.0	2.4	0.0
311	13	6.4	51.5	11.7	12.9	5.2	19.0	37.6	0.0	10.9	21.3	42.0	66.0	0.0	0.0	0.0	0.0	2.6	0.0
312	2	7.0	74.6	11.5	15.0	2.8	23.0	38.5	0.0	13.4	28.0	62.9	101.9						
314	2	6.9	68.5	11.2	12.3	0.0	18.6	38.7	0.0	17.4	26.9	60.2	112.3						
315	2	6.7	49.2	11.3	11.4	6.3	24.6	32.7	0.0	9.9	18.4	52.4	71.1						
316	1	6.8	74.4	10.2	12.2	0.0	12.4	36.6	0.0	13.3	21.6	33.8	80.8						
317	2	7.0	76.5	10.6	13.8	0.0	12.6	42.7	0.0	15.7	21.3	42.1	95.3						
318	2	6.8	68.8	10.9	11.8	0.0	16.5	38.1	0.0	17.3	25.6	58.2	111.0						
319	4	6.9	62.2	10.8	11.4	0.0	16.5	37.9	0.0	10.9	22.6	49.6	93.7						
320	5	6.6	47.3	9.4	10.3	0.0	17.3	32.6	0.0	9.9	16.8	43.2	67.8						
321	4	6.8	63.1	10.4	11.1	4.1	16.5	37.7	0.0	13.2	19.4	42.2	81.0						
322	6	6.7	50.1	9.9	12.4	6.4	18.4	38.1	0.0	11.3	20.6	43.5	74.4						
323	2	6.3	51.5	9.8	10.3	8.7	21.3	35.0	0.0	11.7	22.3	43.4	72.0						
325	1	6.9	53.4	9.5	9.5	6.2	19.6	33.3	0.0	3.0	15.6	24.5	41.0						
326	2	6.5	45.8	13.3	10.2	15.5	42.8	34.2	0.0	14.3	32.5	60.4	72.9						
327	5	6.8	52.3	12.7	13.5	17.7	27.6	44.1	0.0	11.9	25.8	73.8	94.1						
328	3	6.4	20.2	8.5	17.1	10.9	13.5	30.5	0.0	6.0	12.5	34.4	40.7						
329	2	6.7	43.8	13.1	13.1	12.5	19.1	37.3	0.0	9.0	19.1	53.0	73.7						
330	3	6.5	55.7	12.2	12.0	24.0	38.5	29.8	0.0	11.7	27.4	77.8	75.8						
331	1		75.8		28.4	69.3	165.2	17.8	0.0	9.2	41.7	81.7	-112.4						
332	2	6.0	40.6	15.7	25.1	41.4	69.8	35.5	0.0	14.5	30.1	133.8	77.6						
334	2	6.1	13.9	13.4	13.2	27.8	32.4	26.4	0.0	8.8	17.3	48.2	27.3						
335	4	7.6	348.1	39.9	18.5	5.3	45.1	46.7	0.0	14.5	78.1	288.3	352.5						
336	9	6.3	49.6	11.1	16.7	24.3	10.3	40.0	0.0	14.1	25.8	60.6	81.7						
337	12	6.4	45.5	12.1	14.5	26.2	17.7	35.2	0.0	10.2	20.5	45.5	57.1						
339	1	7.0	100.6	13.9	11.6	1.1	25.4	55.4	0.0	13.1	27.8	72.1	130.3						
341	5	7.2	105.7	23.2	18.6	0.0	105.8	44.0	0.0	9.7	98.6	114.3	153.9						
342	4	6.9	55.7	16.8	15.7	0.0	76.6	34.4	0.0	8.4	76.2	69.3	95.4						

Site ID	N	pH	ANC	Cond	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BCS	Al	Cu	Fe	Mn	Si	Zn
343	2	6.8	64.3	8.4	12.2	1.6	7.9	35.7	0.0	10.7	16.0	33.3	74.0						
344	1	6.4	56.9	8.3	14.1	0.0	12.5	38.8	0.0	11.4	16.0	32.6	72.2						
350	2	6.9	81.3	12.5	13.0	9.5	14.9	39.7	0.0	14.2	23.3	57.6	97.4						
352	1	7.3	159.0	36.8	19.1	0.0	153.2	79.3	0.0	13.7	125.3	145.1	191.1						
357	3	7.0	105.9	14.7	9.6	5.9	11.7	54.5	0.0	15.7	21.3	83.7	140.2						
358	1	7.0	79.8	12.1	15.9	0.0	9.1	48.8	0.0	10.6	20.2	40.4	95.0						
359	1	6.8	58.7	10.8	11.4	1.8	10.9	39.3	0.0	8.0	10.6	34.7	68.4						
360	2	4.7	-21.3	21.8	12.4	41.5	72.7	14.0	0.0	2.4	28.7	45.7	-35.9						
361	1	4.8	-17.5	26.4	10.4	70.7	74.4	17.9	0.0	3.8	18.7	60.1	-55.0						
362	2	6.9	50.3	9.7	9.5	5.5	17.5	32.8	0.0	10.2	20.5	58.0	89.0						
377	1	7.1	135.3	19.8	16.4	0.0	53.0	72.1	0.0	5.7	54.0	106.8	169.2						
392	1	6.7	53.8	10.9	7.8	2.6	18.4	34.7	0.0	7.3	16.1	46.9	76.2						
472	9	6.2	24.8	11.5	14.6	17.9	32.7	26.3	0.0	7.9	20.9	48.3	43.0	0.1	0.0	0.0	0.0	2.4	0.0
473	8	5.6	5.5	18.6	15.1	35.4	75.8	21.1	0.0	5.6	45.3	92.9	35.9	0.1	0.0	0.0	0.0	1.5	0.0
474	15	6.2	45.3	13.0	17.2	11.5	33.4	29.6	0.0	10.6	20.6	50.0	47.8	0.1	0.0	0.0	0.0	2.6	0.0
475	11	6.2	26.8	11.5	17.6	15.7	29.3	31.8	0.0	9.7	19.9	41.0	39.1	0.0	0.0	0.0	0.0	2.5	0.0
479	12	6.4	57.0	11.7	14.5	4.6	18.4	37.6	0.0	11.3	22.6	41.5	63.6	0.0	0.0	0.0	0.0	2.6	0.0
480	11	6.5	74.3	13.6	11.9	1.9	22.9	42.7	0.0	12.5	27.5	44.6	84.7	0.0	0.0	0.0	0.0	3.2	0.0
481	12	6.4	74.1	19.2	12.9	0.0	60.4	39.9	0.0	14.8	46.4	55.2	84.2	0.0	0.1	0.0	0.0	3.1	0.2
482	11	6.4	81.4	14.7	13.3	3.5	22.6	42.7	0.0	12.5	36.3	45.5	95.1	0.0	0.0	0.0	0.0	3.1	0.0
483	11	6.5	74.6	14.7	12.5	1.4	30.8	43.6	0.0	12.9	34.2	47.9	87.7	0.0	0.0	0.0	0.0	3.1	0.0
484	12	6.3	43.9	10.7	12.5	6.9	16.6	34.7	0.0	10.2	18.6	34.2	59.2	0.0	0.0	0.0	0.0	2.5	0.0
485	13	6.4	64.2	12.1	12.6	2.7	16.2	37.8	0.0	11.5	23.2	40.2	77.6	0.0	0.0	0.0	0.0	2.8	0.0
486	1	6.8	55.9	9.0	11.2	4.6	17.5	33.2	0.0	9.6	22.3	59.5	91.1						
488	20	6.3	37.6	12.5	14.6	12.2	24.1	36.3	0.0	10.4	20.8	39.9	56.1	0.0	0.0	0.0	0.0	2.5	0.0
489	18	7.3	633.9	63.2	18.1	11.6	44.8	47.8	0.0	14.5	126.0	499.8	596.8	0.0	0.0	0.0	0.0	3.1	0.0
492	31	6.3	33.7	17.7	13.0	45.5	45.6	31.8	0.0	9.4	37.9	69.2	48.1	0.0	0.0	0.0	0.0	2.3	0.0
493	9	6.4	69.1	12.2	15.5	7.2	19.6	43.0	0.0	13.0	18.0	43.4	69.7	0.0	0.0	0.0	0.0	3.2	0.0
495	1	7.1	68.7	11.3	12.6	8.2	12.1	42.9	0.0	14.4	24.6	75.5	124.6						
496	1	7.1	78.9	11.6	13.1	0.0	8.8	47.2	0.0	13.8	27.3	69.3	135.7						

Appendix 8. Median Fish Metrics for Stream Survey Sites from 1990 to 2009 for Brook and Rainbow Trout, YOY and Adults.

(trout density (Den) and biomass (Biom) are in fish/100 m² and kg/ha, respectively).

Site ID	Brook Trout							Rainbow Trout						
	N	YOY Den	Adult Den	YOY Biom	Adult Biom	YOY K	Adult K	N	YOY Den	Adult Den	YOY Biom	Adult Biom	YOY K	Adult K
ABC-1								7	0	0.05	0	0.37	0.97	0.98
ABC-2								9	12.00	5.69	9.35	41.75	1.00	0.94
ABC-3								10	6.26	3.14	4.70	26.97	0.99	0.94
ABC-4								10	0.85	0	0.98	0	1.01	1.05
ACB-1	2	0.90	1.22	0.29	3.27	1.03	0.93	2	0	3.26	0	9.67	1.00	0.93
ACB-2	1	0	1.52	0	6.06		0.93	2	0.15	6.24	0.01	14.07	0.89	0.94
ACB-3	5	7.55	5.45	1.51	9.58	0.89	0.92	2	0	3.38	0	10.10	0.82	0.94
ACB-4	5	8.69	7.68	2.05	12.51	0.87	0.91	1		0.33		5.81		1.00
ACB-5	1	0.30	2.43	0.06	7.93	0.88	0.98	1		0.95		4.98		0.98
ACB-6	1	0.25	1.52	0.10	5.95	1.46	0.91	2	0	1.64	0	6.84		0.98
ADB-1	9	3.75	12.29	0.64	25.60	1.08	0.97	4	0	0.66	0	5.45		0.99
ALC-1	3	0	0.76	0	3.78	0.86	1.04	2	0	0.15	0	0.40		0.83
ALC-2	3	0	0.38	0	6.39		1.05	1	0	0.75	0	1.68		0.85
ALC-3	2	0	0.16	0	1.15	0.80	0.90							
ANC-1								10	4.10	3.39	1.43	13.44	1.05	1.00
BEC-1	17	3.11	2.66	0.69	6.38	0.97	0.96	17	1.70	6.06	0.34	21.08	0.91	0.91
BEC-2	16	2.02	4.15	0.71	9.56	0.93	0.95	16	2.87	5.42	0.54	18.97	0.91	0.92
BEF-0	1	0.12	0	0.03	0	1.23		1	4.58	2.77	0.46	10.75	1.19	0.98
BEF-1	7	0.83	1.34	0.31	4.19	1.01	0.94	7	2.70	4.83	0.47	20.12	1.22	1.02
BEF-2	8	2.99	6.13	0.53	14.96	1.06	0.91	8	0	3.39	0.01	11.13	1.12	0.97
BGP-1	1	1.15	5.35	0.15	11.35	0.95	0.94	1	0	1.91	0	8.51		0.97
BGP-2	1	4.92	18.60	0.64	39.07	0.99	0.93							
BIB-1								2	1.37	7.39	0.73	35.70	1.10	0.95
BLK-1	1	0	0	0	0		0.66	13	7.44	3.87	0.81	10.38	1.02	0.94
BLK-2	1		0.33		0.44		0.76	13	2.92	5.35	0.29	18.69	1.06	0.95
BLK-3								11	3.43	5.75	0.44	15.32	0.96	0.98
BRC-0								1	0.61	3.64	0.25	13.20	1.05	1.07

Site ID	Brook Trout							Rainbow Trout						
	N	YOY Den	Adult Den	YOY Biom	Adult Biom	YOY K	Adult K	N	YOY Den	Adult Den	YOY Biom	Adult Biom	YOY K	Adult K
BRC-18	2	5.56	4.22	1.96	9.21	0.99	0.96	1	0	4.19		15.08	0.96	0.98
BRC-1C								3	0	1.08	0.05	6.71	0.95	1.11
BRC-33	2	7.11	9.25	2.38	20.50	1.04	0.96	2	0.99	3.72	0.49	16.10	1.53	0.97
BRC-9	1	0	0.27	0	0.15	0.93		1	0.56	4.52	0.32	20.70	1.14	0.92
BUN-1	19	10.17	20.11	3.80	54.30	0.97	0.97							
BUN-2	20	14.37	29.49	4.22	63.64	0.98	0.96							
BUN-3	20	18.15	28.26	4.65	55.94	0.97	0.98							
CAN-1								9	0.66	1.74	0.05	8.33	1.01	1.00
CAN-1M								1	0	0.99	0	6.39		1.07
CAN-2								8	0.18	3.32	0.06	16.62	1.05	1.01
CAN-3M								1	0	2.45	0	8.53		0.92
CAT-1	7	0.03	0.07	0.03	0.18	0.87	0.90	15	4.65	3.82	2.75	26.34	1.02	0.97
CAT-2	2	0.37	0.31	0.35	0.81	0.96	0.94	15	3.86	4.12	4.10	23.91	1.06	0.97
CAT-3	3	0.05	0.10	0.04	0.27	1.07	0.84	15	4.00	4.55	3.38	20.85	1.05	0.95
CAT-4	10	0.12	0.11	0.09	0.24	1.06	0.90	16	4.07	5.26	2.12	23.11	1.06	0.94
CHC-1	3	1.32	3.80	0.28	10.10	1.04	0.97							
COK-1	4	6.83	4.08	1.71	9.74	1.10	0.93	4	1.19	9.28	0.17	27.14	0.95	0.90
COS-1	17	0.21	0.66	0.07	2.06	0.98	0.97	17	0.97	4.51	0.16	17.76	1.06	0.97
COS-1A	1	0.22	2.59	0.01	8.62	0.95	0.92	1	2.80	0.43	1.04	1.26	0.73	0.88
COS-2	15	5.40	8.11	1.55	26.10	1.08	1.02							
COS-2A	1	3.50	6.29	1.29	16.74	1.03	0.94	1	0.28	3.50	0.02	15.07	0.88	0.97
DES-1M	3	4.63	6.94	1.34	13.73	0.92	0.89	3	0	1.31	0	5.33		1.02
DES-2M	3	6.35	4.16	1.91	7.53	0.89	0.96							
DES-3M	3	8.01	6.76	2.00	15.87	0.87	0.90	1	0.48	0.80	0.16	2.13	0.91	1.01
DES-4M	3	5.35	7.72	1.39	15.29	0.83	0.89	3	0.79	0.60	0.25	1.99	0.94	0.99
DPC-1	2	6.93	5.97	1.87	15.40	0.94	0.95	2	0.38	1.39	0.02	4.89	0.91	0.98
DPC-2	2	7.60	8.87	2.04	16.54	0.92	0.89	2	1.09	3.95	0.13	16.36	1.12	0.95
DPC-3	2	7.54	27.72	1.40	60.37	0.91	0.88							
DUN-0	1	1.22	0.81	0.33	1.76	0.89	0.84	1	0.41	2.64	0.11	10.51	1.10	0.96
DUN-1	3	3.70	4.79	1.20	13.82	0.80	0.91	3	0	1.31	0	9.87		0.98
DUN-2	12	3.24	4.88	1.07	12.72	1.00	0.99	4	0	0.62	0	4.34	0.99	1.04
DUN-3	11	6.04	7.22	1.82	15.76	1.02	0.96	2	0	0.65	0	5.13		1.03
DUN-4	1	10.37	11.18	2.70	25.93	0.96	0.90							

Site ID	Brook Trout							Rainbow Trout						
	N	YOY Den	Adult Den	YOY Biom	Adult Biom	YOY K	Adult K	N	YOY Den	Adult Den	YOY Biom	Adult Biom	YOY K	Adult K
EKT-1N								2	1.20	7.37	1.15	24.92	0.98	1.00
EKT-2N								2	0.21	0.90	0.11	6.15	0.85	1.13
EKT-3N	2	0.17	0	0.08	0	1.03	0.98	1	0.72	1.45	0.49	8.80	1.02	0.93
EKT-4N	2	0.66	0.09	0.22	0.32	0.93	1.04	2	0.48	1.21	0.62	8.62	1.29	1.04
FCP-1	1	0.22	0.11	0.19	0.13		0.90	2	0.57	7.30	0.13	31.09	1.05	0.92
FCP-2	2	0.10	0.34	0.09	0.98		0.97	2	1.14	6.33	0.12	26.27	0.96	0.89
FCP-3	4	1.90	3.84	0.35	9.74	0.80	0.86	4	3.43	3.62	0.25	14.54	0.92	0.88
FCP-4	4	4.71	6.54	1.13	14.46	0.87	0.90	4	0.17	2.89	0.01	16.25	0.85	0.98
FLT-1	17	21.02	30.66	4.74	46.55	0.98	0.95							
GBC-1	1	4.28	11.49	0.64	25.27	0.76	0.92	1	0.90	0.68	0.10	3.26	0.65	1.06
GBC-2	1	8.36	32.45	1.34	61.01	1.21	0.89							
GRC-1	1	0.67	3.60	0.16	5.98	0.88	0.83	1	1.07	8.54	0.18	34.07	0.93	0.93
GRC-2	1	1.87	7.47	0.17	14.86	0.64	0.92							
HAZ-1	2	0	0.06	0	0.17		0.91	5	2.38	2.97	1.44	19.72	1.07	0.99
HAZ-1N	8	1.15	1.51	0.48	4.95	0.92	0.92	8	2.18	3.58	1.23	19.89	1.11	0.98
HAZ-2	12	5.49	9.24	1.69	22.01	0.93	0.94	12	0.24	1.89	0.07	7.78	1.10	1.02
HAZ-2N	2	1.25	2.42	0.54	6.51	0.91	0.89	2	2.69	6.81	0.91	28.69	0.99	0.95
HAZ-3	12	10.26	11.96	3.05	28.75	0.96	0.96							
HAZ-3N	8	5.51	7.41	1.88	15.71	0.98	0.94	8	1.08	2.45	0.38	9.58	1.10	0.99
ICC-1	3	4.86	5.06	1.75	13.26	0.87	0.91							
ICC-1N	14	0.98	1.45	0.34	3.73	1.03	0.95	14	0.08	0.54	0.00	2.35	1.04	1.11
ICC-2	17	5.42	5.74	1.50	14.98	0.97	0.95	9	0	0.15	0	1.20	1.06	0.98
ICC-3	3	3.79	5.45	1.59	19.40	0.93	0.90							
ICC-3N	15	4.15	11.05	0.91	22.77	1.06	0.96							
IFP-0	2	0.49	2.03	0.06	6.53	0.94	0.86	3	4.72	6.88	0.66	20.37	1.00	0.93
IFP-15	2	2.01	0.53	1.27	2.17	1.06	1.03							
IFP-5	2	12.81	3.63	5.35	14.02	1.11	1.02							
JAK-1								13	2.34	6.41	0.18	22.09	1.11	1.01
JAK-2								10	0.82	6.65	0.07	25.29	1.09	0.99
JON-1								1	2.85	3.23	1.11	12.29	1.07	0.99
JON-2								2	5.26	4.73	1.06	19.33	1.04	1.01
JON-3								1	0.77	7.49	0.21	27.12	0.96	0.92
JON-4								1	10.29	5.97	2.88	24.65	0.97	0.95

Site ID	Brook Trout							Rainbow Trout						
	N	YOY Den	Adult Den	YOY Biom	Adult Biom	YOY K	Adult K	N	YOY Den	Adult Den	YOY Biom	Adult Biom	YOY K	Adult K
KAN-1	11	4.34	9.46	0.81	19.32	0.97	0.94							
KEB-1	9	2.37	7.36	0.55	15.75	1.06	0.94							
LBR-1								16	0	2.93	0	13.26	0.96	1.00
LBR-2	1	0	2.34	0	13.09	1.24	0.98							
LBTRA-1	7	2.45	19.89	0.66	35.01	0.96	0.92	2	0.49	0.74	0.02	2.08	0.90	0.90
LBTRA-2	7	3.88	9.94	1.10	18.59	0.91	0.94	1	0	0.41	0	1.34		0.89
LBTRA-3	7	3.08	14.53	0.40	18.08	0.91	0.92							
LBTRB-1	7	4.01	3.90	0.79	6.86	0.94	1.00							
LCP-1	1	5.55	1.85	21.49	5.28	1.17	1.18	1	0	0.14	0	0.38		
LCP-11								2	5.39	7.25	1.58	24.86	1.04	0.94
LCP-33	1	0	0.06	0	0.18		0.88	2	5.94	6.33	2.39	20.77	1.12	0.95
LCP-68								1	3.26	17.71	0.52	43.74	0.95	0.97
LCT-1	2	1.34	2.98	0.31	7.11	0.95	0.87	2	2.50	4.75	0.53	16.82	0.83	0.89
LCT-1M	1	1.39	3.19	0.43	6.63	0.94	0.88	1	1.20	7.37	0.25	36.26	1.00	0.98
LCT-2	3	1.72	1.72	0.34	3.70	0.96	1.00	3	1.35	2.08	0.47	9.06	0.98	0.98
LCT-2M	1	1.82	2.83	0.51	6.65	0.94	1.00	1	2.02	5.26	0.38	14.98	0.95	0.93
LCT-3	3	1.61	3.22	0.53	9.94	0.98	0.97	3	0.46	4.15	0.11	14.80	1.09	0.98
LCT-4	3	4.01	3.47	1.39	7.82	1.11	0.97	3	1.63	3.62	1.23	11.70	1.10	0.96
LEC-0	8	1.09	0.86	0.24	2.63	0.97	0.98	8	0.54	4.25	0.03	19.80	1.01	1.03
LEC-1	8	2.69	0.96	0.76	4.19	0.99	1.05	4	0	0.21	0	1.81	1.01	1.02
LEC-2	5	2.85	1.48	0.78	5.72	1.05	1.05	3	0.47	0.40	0.02	3.53	0.88	1.04
LEC-3	2	5.41	0.94	1.60	4.83	1.07	1.05	1	0	0.25	0	0.86		1.09
LEC-4	1	2.40	0.60	0.82	2.19	1.06	1.01							
LEC-5	2	7.09	2.15	2.22	12.71	1.01	1.12	1	0	0.19	0	2.29		0.95
LEC-6	1	5.98	1.42	1.85	8.88	0.98	1.08							
LEC-7	1	0.55	0.37	0.23	1.57	0.97	1.03							
LEC-8	1	0.68	1.82	0.25	9.29	1.13	1.08							
LEC-9	4	2.77	6.23	0.66	14.48	1.12	1.02							
LEC-10	10	3.74	7.54	1.30	17.55	1.08	0.98	2	0	0.15	0	0.38		1.01
LEC-11	1	2.82	1.54	0.84	6.05	1.15	1.01							

Site ID	Brook Trout							Rainbow Trout						
	N	YOY Den	Adult Den	YOY Biom	Adult Biom	YOY K	Adult K	N	YOY Den	Adult Den	YOY Biom	Adult Biom	YOY K	Adult K
LEC-12	1	1.61	4.30	0.45	16.32	1.27	0.96							
LEC-13	1	0	1.30	0	4.46		0.95							
LEC-14	1	0.47	0	0.13	0	0.97								
LEC-15	1	1.17	0.17	0.29	0.83	1.08	1.03							
LEC-16	1	0.22	1.96	0.07	6.31	1.04	1.02							
LEC-17	7	3.05	5.80	0.67	18.84	1.14	0.99							
LEC-19	1	0.13	0	0.05	0	0.88								
LEC-20	1	0.82	0.21	0.25	1.48	1.01	1.10							
LEC-21	1	0.41	0.41	0.12	2.46	0.92	1.04							
LEC-22	1	0.53	0.88	0.14	3.27	0.97	1.03							
LEC-23	1	0	2.20	0	12.47		1.03							
LEC-24	8	3.49	8.56	0.88	25.32	1.07	0.99							
LEC-25	1	0	0.56	0	2.78		1.09							
LJC-1	1	0.58	1.45	0.09	3.95	0.79	0.98	1	0	2.03	0	6.89		0.95
LOB-0	12	2.51	5.84	0.53	12.49	0.91	0.91	12	0.46	3.55	0.05	13.37	1.00	0.92
LOB-1	16	9.10	4.58	2.85	10.42	1.02	0.98	2	0	0.29	0	1.33		0.78
LOB-2	16	8.15	7.63	1.91	16.68	1.00	0.98	3	0	0.18	0	2.50		0.82
LOB-3	15	7.22	8.96	2.20	19.47	1.02	1.01	2	0	0.49	0	3.16		0.74
LOB-4	7	6.42	9.70	2.82	19.60	0.98	0.98	2	0	0.23	0	1.00		1.22
LOB-5	7	8.02	11.62	1.92	24.70	0.99	0.97	2	0	0.59	0	1.86	1.07	1.00
LOB-6	7	9.12	12.61	3.08	28.00	0.98	1.00	2	0	0.19	0	0.67		0.89
LOB-7	7	12.71	14.96	2.67	30.53	0.94	0.96	2	0.17	0.87	0.04	2.33	1.11	0.98
LOB-8	7	6.37	15.95	1.61	30.29	0.93	0.96	5	0.14	0.48	0.02	1.20	0.94	0.97
LOB-9	7	9.21	17.30	3.29	33.16	1.00	0.97	3	0.36	0.90	0.07	2.29	0.99	1.01
LOB-10	7	7.88	8.47	2.53	22.69	1.01	1.00	5	0	0.93	0	3.90	1.10	1.05
LOB-11	8	6.09	11.54	1.75	25.58	1.00	0.97	6	0.34	0.42	0.04	1.89	0.82	0.90
LOB-12	8	5.41	9.10	1.58	20.22	0.95	0.97	4	0.19	0.88	0.01	3.63	0.88	0.99
LOB-13	8	6.24	10.54	1.66	20.08	0.97	0.96	4	0.24	1.27	0.04	4.29	0.97	1.00
LOB-14	7	3.31	14.10	1.15	26.08	1.00	0.97	4	0.22	1.20	0.04	5.57	1.10	0.90
LOB-15	7	5.38	10.26	1.29	18.67	0.93	0.97	4	0	1.31	0	5.07	1.00	1.01
LOB-16	7	3.36	11.15	1.10	21.53	0.97	0.95	4	0	1.27	0	4.93	1.10	0.85
LOB-17	7	8.77	11.00	2.76	22.04	0.92	0.96	4	0	0.48	0	1.56	0.90	0.95
LOB-18	7	10.97	14.03	2.52	30.80	0.94	0.94	5	0	0.60	0	2.16	0.98	0.89

Site ID	Brook Trout							Rainbow Trout						
	N	YOY Den	Adult Den	YOY Biom	Adult Biom	YOY K	Adult K	N	YOY Den	Adult Den	YOY Biom	Adult Biom	YOY K	Adult K
LOB-19	8	5.32	16.63	1.53	34.67	1.03	0.97	3	0.33	1.02	0.01	4.34	0.77	0.84
LOB-20	8	5.28	12.06	1.23	27.65	0.93	0.90	5	0.22	0.41	0.01	1.28	0.79	0.91
LOB-21	8	7.14	11.11	1.75	22.66	0.94	0.92	3	0	1.58	0	8.04	0.90	0.87
LOB-22	7	6.09	12.19	1.43	24.50	1.00	0.93	2	0.40	1.99	0.03	8.62	0.91	0.92
LOB-23	7	9.31	12.88	2.10	23.45	0.98	0.93	3	0	0.72	0	1.50	0.90	0.94
LOB-24	7	8.18	13.10	2.44	22.85	0.94	0.95	3	0	1.27	0	5.02	0.87	1.00
LOB-25	7	5.42	11.28	1.52	19.28	0.96	0.91	2	0.66	2.58	0.03	9.46	0.86	0.95
LOB-26	7	7.67	12.15	1.77	24.44	0.98	0.91	2	0	1.21	0	3.28	0.66	0.89
LOB-27	7	9.62	22.69	2.87	44.67	0.94	0.92	2	1.14	3.19	0.09	9.07	1.09	0.89
LOB-28	7	8.36	15.67	2.26	35.31	0.94	0.96	3	0	0.37	0	1.64	0.77	0.92
LOB-29	7	3.84	15.24	1.23	34.58	0.99	0.95	2	0	1.68	0	6.12		0.95
LOB-30	7	3.52	20.16	1.16	42.47	0.94	0.93	2	0.81	3.92	0.15	13.12	1.11	0.94
LOB-31	7	5.24	18.75	2.04	44.41	0.91	0.93	3	0	4.38	0	12.86	1.02	0.93
LOB-32	8	3.87	15.65	1.16	30.12	0.94	0.93	5	0	0.49	0	2.28	1.17	0.92
LOB-33	8	7.24	23.04	2.39	36.41	0.99	0.89	4	0.17	1.17	0.01	4.56	1.05	0.91
LOB-34	8	2.79	23.49	0.56	44.54	0.86	0.89	4	0	1.29	0	7.82		0.93
LRV-0								3	0.04	0.45	0.04	6.08	1.12	1.03
LRV-1								14	2.34	2.51	1.58	20.66	0.99	0.91
LRV-2								13	5.11	4.60	4.96	26.67	0.97	0.91
LRV-3								11	4.97	7.90	0.83	41.23	0.99	0.91
LRV-3N								6	4.73	5.88	3.80	39.20	1.03	0.93
LRV-5	1		0		0	0.64		1		4.90		20.62	0.80	0.91
LRV-6	1	2.66	0.16	0.72	0.64	0.95	0.85	1	0	4.53	0	21.97		1.03
LRV-7	1	2.75	0.36	0.77	1.09	0.82	0.90	1	1.44	5.51	0.19	27.32	0.64	0.98
LRV-8	1	3.47	1.03	0.87	4.32	0.88	0.89	1	0	3.34	0	17.32		1.00
MAC-1	1	1.71	1.71	0.27	7.42	0.90	1.05							
MAC-4								1	3.55	8.16	1.06	20.33	1.07	0.94
MAN-1	2	0.23	1.08	0.07	5.04	1.08	1.01	2	2.23	0	0.60	0	0.94	
MAN-2	5	2.71	3.17	0.76	8.91	1.13	1.09	5	0.44	0.39	0.28	1.89	0.96	0.88
MAN-3	9	3.10	3.69	1.24	9.49	1.02	1.04	4	0.18	1.14	0.01	3.96	0.89	0.98
MAN-4	2	6.64	1.74	4.07	7.12	1.00	0.98	4	1.22	0.99	0.28	1.88	1.04	0.94
MAN-5	2	8.44	3.55	4.08	16.05	1.06	1.03	3	0.99	1.83	0.34	3.85	0.94	0.92
MAN-6	12	4.06	2.77	1.16	11.14	0.99	1.00	5	1.17	0.29	0.63	1.28	0.98	0.93

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	N	YOY Den	Adult Den	YOY Biom	Adult Biom	YOY K	Adult K	N	YOY Den	Adult Den	YOY Biom	Adult Biom	YOY K	Adult K
MAN-7	2	3.40	1.51	2.00	5.96	1.06	0.98	5	2.16	0.28	0.71	1.22	1.00	0.95
MAN-8	11	6.77	5.55	2.33	16.05	1.00	1.03	6	1.53	2.06	0.03	4.60	0.94	0.86
MAN-9	2	0.75	2.91	0.43	15.23	0.95	1.03	5	0.54	3.62	0.03	7.96	1.00	0.92
MEG-1	3	0	0.61	0	4.71	1.14	1.02							
MEG-2	3	0.50	1.75	0.25	15.11	0.98	0.99							
MEG-3	4	0.55	1.73	0.25	12.07	0.92	0.93							
MIL-1								9	3.60	2.05	3.01	10.95	1.03	0.92
MIL-2								10	1.99	2.77	1.80	10.23	0.99	0.99
MPLP-0								1		0.31		5.10		0.99
MPLP-1								2	1.36	2.14	0.53	12.22	1.04	1.03
MPLP-2								1		4.00		22.16		1.05
MPLR-4								1	6.68	7.03	2.40	28.00	1.09	0.96
NWP-3								8	0.54	6.53	0.16	24.54	1.10	1.04
OCO-3	1	0	0.05	0	0.19		0.77	1	2.40	3.59	0.72	14.30	1.01	0.95
PAL-1	2	1.45	1.69	0.45	5.33	0.98	0.96	3	5.13	9.45	1.24	31.67	0.94	0.92
PAR-1								2	0.23	4.89	0.14	14.91	1.04	0.91
PLK-1	1	1.09	1.37	0.31	4.44	0.89	0.93							
PLK-2	1	9.19	2.73	3.49	9.07	0.86	0.92							
PLK-3	2	6.09	1.05	2.81	3.17	1.01	0.99	1	0	0.23	0	2.80		0.99
PLK-4	1	3.78	2.65	1.44	8.42	1.02	0.97							
PLK-5	1	0	1.22	0	5.34		1.05							
PLK-6	1	3.22	1.07	1.19	3.61	0.95	1.02							
PLK-7	1	1.69	1.48	0.62	5.37	0.90	1.06							
PLK-8	1	0.98	3.44	0.37	14.52	1.04	1.04							
PLK-9	1	1.70	1.36	0.53	5.17	1.11	0.97							
PLK-10	2	3.56	7.85	1.48	28.62	1.02	0.98							
PLK-11	1	6.23	0.24	3.05	0.96	1.09	1.00							
PLK-12	1	1.98	1.32	0.79	11.02	1.09	0.97							
PLK-13	1	1.67	0.67	0.77	4.15	1.12	1.03							
PLK-14	1	1.78	0.30	1.19	3.14	1.16	1.05							
PLK-15	1	0.33	0	0.16	0	1.01								
PTH-1	4	4.07	4.94	0.83	10.96	0.92	0.92	4	3.38	9.73	0.61	32.25	1.00	0.91
PTH-2	4	5.55	3.36	0.81	6.01	0.90	0.95	4	1.93	4.26	0.51	12.99	0.88	0.91

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	N	YOY Den	Adult Den	YOY Biom	Adult Biom	YOY K	Adult K	N	YOY Den	Adult Den	YOY Biom	Adult Biom	YOY K	Adult K
RFC-1	1	0	0.13	0	1.23		0.95	11	1.34	9.10	0.22	39.87	1.02	0.96
RFC-1N								1	0.17	8.14	0.00	42.25	1.10	0.91
RFC-2	1	0	0.22	0	1.00		0.89	10	1.25	9.33	0.01	37.77	1.05	1.04
ROC-1	6	0.68	0.90	0.28	3.23	1.00	0.98	6	0.19	1.22	0.01	7.45	1.08	0.97
ROC-2	13	0.44	1.78	0.11	4.87	0.96	0.97	13	0	0.67	0	3.03	0.97	0.96
ROC-3	4	0.21	2.80	0.07	6.94	1.30	0.97	3	0	0.82	0	4.34		1.01
ROC-5	3	4.97	4.60	1.49	12.85	1.00	0.95	3	0.43	0.18	0.06	1.15	0.97	1.03
ROC-6	20	1.25	3.38	0.37	12.49	1.07	1.05	5	0	0.15	0	1.25	1.36	1.00
ROC-7	20	1.14	3.58	0.31	8.67	1.06	0.98	1	0	0.14	0	1.10		1.06
RPR-1	2	1.27	0.13	0.03	0.39		0.95	3	0.54	2.34	0.01	13.28	0.63	1.01
RPR-2	17	0.81	1.45	0.14	4.78	1.01	0.94	17	0.14	3.94	0.02	14.72	0.97	1.02
RPR-5	18	2.10	5.41	0.29	18.25	1.04	0.94	2	0	0.84	0	3.70		1.10
SAM-1	7	0.95	2.72	0.75	13.25	1.08	1.05	8	1.32	3.58	0.53	25.40	1.05	1.01
SAM-1M								3	1.57	5.56	0.22	26.84	1.04	1.00
SAM-2								5	1.17	4.78	0.17	26.78	1.01	1.01
SAM-2M								3	2.60	9.35	0.24	42.83	0.98	1.00
SAM-3	8	0.12	0.28	0.05	2.20	1.02	1.08	11	1.67	3.48	0.43	19.82	1.03	1.02
SAM-3M	1	0	0.16	0	0.23		0.91	3	0.73	11.04	0.10	45.23	1.01	0.97
SAM-4	1	9.72	16.94	2.63	32.86	1.02	0.94							
SAM-4M								3	1.48	5.22	0.15	23.90	1.02	1.07
SAM-5	14	0.83	1.91	0.19	6.12	0.97	0.91	10	0.55	4.14	0.09	21.23	0.98	0.98
SAM-5M	1	0.58	2.07	0.05	6.28			3	2.37	5.76	0.26	23.45	0.96	1.01
SAM-6	14	2.73	11.84	0.52	28.45	1.04	0.92	5	0	0.39	0	2.52		1.07
SAM-7	2	1.66	6.91	0.14	19.68	1.19	0.97							
SAM-8	2	1.74	8.06	0.16	25.36	1.22	0.95							
SAM-C1								7	6.70	3.74	3.69	15.47	1.02	0.95
SAM-C2								8	7.26	4.32	3.25	17.46	1.04	0.95
SAM-C3	2	0.57	0.19	0.12	1.38	0.86	0.78	8	2.17	3.22	0.48	16.56	1.07	0.96
SAM-S5								2	3.92	2.13	3.67	15.19	1.11	1.07

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SAM-S6								2	6.65	2.25	5.42	15.09	1.04	0.98
SAM-S18								2	3.00	1.61	2.69	14.94	0.96	1.01
SAM-S19								2	2.38	2.38	1.81	14.63	1.03	0.94
SAM-S25	1	0.20	0	0.11	0		0.90	1	2.15	5.08	1.76	18.89	1.05	0.88
SAM-S26								1	4.75	4.22	4.46	17.18	1.17	0.93
SAM-S33	1	2.65	3.67	1.22	7.57	0.83	0.81	1	5.51	1.43	3.53	9.57	1.03	0.96
SAM-S39	1	2.36	4.13	0.85	8.18	0.82	0.80	1	2.16	3.15	1.38	13.91	1.01	0.89
SIL-1	14	2.54	6.17	0.51	14.23	0.86	0.94							
SIL-2	1	11.37	6.88	2.05	14.30	0.73	0.88							
SIL-3	1	13.24	5.22	2.52	12.05	0.77	0.93							
SIL-4	5	6.79	8.74	1.08	19.90	0.81	0.91							
SIL-5	4	12.98	8.89	2.58	14.57	0.82	0.88	1	0	0.16	0	1.13		0.86
SIL-6	4	8.59	7.65	2.74	18.38	0.89	0.89							
SIL-7	1	9.38	11.15	2.16	32.34	0.81	0.92							
SIL-8	1	12.06	15.20	2.41	43.79	0.79	0.90							
SIL-9	14	3.01	9.12	0.61	24.70	0.90	0.90							
SIL-10	13	4.26	6.32	1.01	13.93	0.91	0.93							
STK-1	15	1.29	2.38	0.28	8.95	0.96	0.96	10	0.07	0.64	0.02	3.96	0.87	0.99
STK-2	2	2.60	8.33	0.16	22.45	0.80	0.88	1	0	0.65	0	2.46		0.99
STK-3	2	1.37	9.33	0.31	21.87	0.63	0.89							
STR-1	5	0.12	0.08	0.11	0.86	1.05	0.88	10	4.66	2.71	1.95	15.18	1.09	0.97
STR-2	11	0.65	0.83	0.42	3.91	1.03	0.92	11	1.55	3.30	0.87	15.40	1.11	0.99
TAY-1	12	4.05	4.48	1.68	16.30	1.06	1.03							
TAY-11	12	5.10	6.07	1.20	12.12	0.99	0.96							
TAY-2	1	10.21	3.19	4.08	18.76	1.02	1.09							
TAY-3	1	8.53	3.00	3.41	15.46	1.03	1.01							
TAY-4	13	4.74	6.99	1.18	26.81	1.05	0.97							
TAY-5	1	15.78	2.67	5.21	15.21	1.03	0.98							

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	N	YOY Den	Adult Den	YOY Biom	Adult Biom	YOY K	Adult K	N	YOY Den	Adult Den	YOY Biom	Adult Biom	YOY K	Adult K
TAY-6	1	11.51	4.27	4.03	22.22	1.01	1.00							
TAY-7	1	11.40	2.39	3.19	9.99	1.03	0.99							
TAY-8	1	6.27	2.51	1.69	7.50	1.03	0.98							
TAY-9	12	4.05	6.27	1.08	14.01	1.04	1.00							
TAY-10	1	3.38	2.37	1.32	5.28	1.06	0.97							
THD-C1								6	6.25	5.28	3.20	23.74	1.04	0.94
TOM-1	1	1.67	8.19	0.40	18.50	0.82	0.97							
TOM-2	1	1.30	16.33	0.30	33.96	0.84	0.96							
TWC-1								1	12.30	4.50	4.92	12.14	1.02	0.90
WAL-1	1	2.22	7.76	0.75	14.52	0.94	0.93	1	0.44	3.10	0.08	14.72	0.81	0.98
WAL-1N	7	4.69	2.90	1.50	6.31	0.97	0.95	7	2.65	2.80	1.00	7.66	1.03	0.96
WAL-2	1	2.23	2.71	0.76	7.26	0.86	0.93							
WCP-1	13	0.43	0.94	0.08	3.40	1.07	0.96	14	0.37	3.52	0.02	12.41	1.13	0.96
WCP-2	14	1.67	3.96	0.39	11.01	1.08	1.01	14	0	0.84	0	4.05	1.08	0.99
WIN-1	3	2.95	1.26	0.61	3.27	0.88	0.95	5	0.33	3.66	0.12	9.55	0.96	0.94
WIN-2	4	8.43	3.28	2.36	9.20	1.07	1.05	2	0.71	1.58	0.61	4.24	1.18	1.05
WIN-3	4	9.40	5.45	2.61	8.67	1.08	1.01	2	0.25	1.67	0.15	4.72	0.99	1.00
WIN-4	4	11.13	10.33	2.51	14.46	1.06	0.98	2	2.97	1.91	1.72	4.24	1.01	0.95
WPLP-0	1	0.56	0.11	0.51	0.82	1.14	1.08	1	1.78	2.33	1.08	22.71	1.20	0.98

Appendix 9. Stream Sites from the Benthic Macroinvertebrates 1990 - 2003 Survey in GRSM.

Site ID	coordX	coordY	Watershed	Location	Survey years
ABAB01I&M	234178	3944016	Abrams Creek	Confluence of Mill Creek and Abrams Creek	1994-2003
ABAB02I&M	241430	3942165	Abrams Creek	Abrams Creek, close to Rabbit Creek Trail	1994-2003
ABKF01I&M	234835	3944892	Abrams Creek	Confluence of Kingfisher Creek and Abrams Creek	1997
BGBB01I&M	307700	3956860	Big Creek	Bettis Branch, just upstream of the confluence of Bettis Branch and Big Creek	1999
BGBG01I&M	309127	3957951	Big Creek	Big Creek, ~2500 m downstream of site BGBB01	1997
BGBX01I&M	308840	3957120	Big Creek	Baxter Creek	1999
BGCB01I&M	308200	3959110	Big Creek	Chestnut Branch	1996, 1999
BGMC01I&M	307029	3956367	Big Creek	Mouse Creek, 75 m upstream of the confluence of Big Creek and Mouse Creek	1999
BKKB01I&M	275260	3952890	Baskins Creek	Confluence of Baskins Creek and Falls Branch	1995-2003
BKKB02I&M	275680	3952740	Baskins Creek	Baskins Creek, 500 m upstream of site BKKB01	1996
BNBU01I&M	303420	3935950	Bunches Creek	Bunches Creek, 300 m upstream of the confluence of Bunches Creek and Flat Creek	1992, 1994-2003
BNBU02I&M	303350	3936880	Bunches Creek	Bunches Creek, 1000 m upstream of site BNBU01	1994-2001
BNFL01I&M	302780	3936410	Bunches Creek	Flat Creek, 880 m upstream of the confluence of Bunches Creek and Flat Creek	1994-2003
BRBF01I&M	290660	3938310	Bradley Fork	Bradley Fork	1998
BRCH01I&M	290434	3939556	Bradley Fork	Chasteen Creek, 500 m upstream of the confluence of Bradley Fork and Chasteen Creek; 1300 m upstream of site BRBF01	1998
BRTA01I&M	289780	3942530	Bradley Fork	Taywa Creek, 860 m upstream of the confluence of Taywa Creek and Bradley Fork	1993-2003

Site ID	coordX	coordY	Watershed	Location	Survey years
CBCM01I&M	301171	3957604	Cosby Creek	Camel Hump Creek, just upstream of the confluence of Cosby Creek and Camel Hump Creek	1996
CBRC01I&M	300160	3959510	Cosby Creek	Rock Creek, upstream of the confluence of Rock Creek and Cosby Creek	1993-1997
CBRC02I&M	299600	3957830	Cosby Creek	Rock creek, around 900 m upstream of site CBRC01	1992, 1994-2003
CNCN01I&M	238058	3948198		Cane Creek, below the confluence with an unnamed stream	1997
CPCP01I&M	283350	3958530		160 m downstream of the confluence of Copeland Creek and Copeland Creek, left fork	1996
CTBE01I&M	305050	3945400	Cataloochee Creek	Beech Creek, upstream of the confluence of Beech Creek and Palmer Creek	1993-2003
CTCC01I&M	312367	3948781	Cataloochee Creek	Cataloochee Creek, 170 m upstream of the confluence of Cataloochee Creek and Little Cataloochee Creek	1984, 1986, 1989-1992, 1994-1995, 1997-2003
CTLB01I&M	305590	3945660	Cataloochee Creek	Lost Bottom Creek, 300 m upstream of the confluence of Lost Bottom Creek and Palmer Creek	1992-2003
CTLB02I&M	304263	3946905	Cataloochee Creek	Lost Bottom Creek, upstream of the confluence with an unnamed stream	1992-1993, 2003
CTLB03I&M	303230	3947300	Cataloochee Creek	Lost Bottom Creek, 1200 m upstream of site CTLB02	1993-2002
CTLBM1I&M			Cataloochee Creek		1992
CTLC01I&M	312347	3949022	Cataloochee Creek	Little Cataloochee Creek, 110 m upstream of the confluence with Cataloochee Creek	1990
CTLD01I&M	311291	3945132	Cataloochee Creek	Lower Double Branch, upstream of the confluence with Upper Double Branch and Cataloochee Creek	1990
CTPC02I&M	308640	3944350	Cataloochee Creek	Palmer Creek, 140 m upstream of the confluence with Rough Fork	1990, 1994-2003

Site ID	coordX	coordY	Watershed	Location	Survey years
CTTA02I&M	304250	3946960	Cataloochee Creek	Lost Bottom, tributary to an unnamed stream, 70 m upstream of the confluence with Lost Bottom Creek, close to site CTLB02	1994-1995
DDDD01I&M	279090	3956050	Dudley Creek	Dudley Creek	1996
DNDN01I&M	293680	3956680	Dunn Creek	Dunn Creek, 2nd order	1996
DPDP01I&M	279950	3929850	Deep Creek	Deep Creek	1994, 1997
DPDP02I&M	280390	3933896	Deep Creek	Deep Creek, 6000 m upstream of site DPDP01	1997
DPDP03I&M	280250	3940335	Deep Creek	Deep Creek, 8500 m upstream of site DPDP02	1997
DPHB01I&M	279400	3928100	Deep Creek	Hammer Branch, upstream of the confluence with Deep Creek and Indian Creek	1997
DPIN01I&M	279830	3927950	Deep Creek	Indian Creek, upstream of the confluence with Deep Creek and Hammer Branch	1997
DPIN02I&M	282130	3932430	Deep Creek	Indian Creek, 1st order	1997
DPPR01I&M	279250	3934920	Deep Creek	Pole Road Creek, 2000 m upstream of site DPDP02	1997
ELAS01I&M	267000	3942340	East Prong Little River	Ash Camp Branch	1993-1994, 1996
ELLR01I&M	261129	3950547	East Prong Little River	East Prong Little River	1994-2001, 2003
ELLR02I&M	268850	3947050	East Prong Little River	East Prong Little River, far upstream of site ELLR01	1994-2003
ELRO01I&M	271000	3944160	East Prong Little River	Rough Creek, 150 m upstream of the confluence with East Prong Little River	1997
ELSI01I&M	267370	3941670	East Prong Little River	Silers Creek, 400 m upstream of the confluence with Fish Camp Prong	1993-2003
FOBC01I&M	266840	3928240	Forney Creek	Bear Creek, upstream of the confluence with Forney Creek	1994
FOBG09I&M	267870	3930800	Forney Creek	Bee Gum Branch, 100 m above Forney Creek	1994
FOCB05I&M	270030	3933760	Forney Creek	Chokeberry Branch, 1st order	1994
FOFO03I&M	272060	3935620	Forney Creek	Forney Creek, above Steeltrap Creek	1994
FOFO04I&M	271170	3934910	Forney Creek	Downstream of the confluence of Steeltrap Creek and Forney Creek	1994

Site ID	coordX	coordY	Watershed	Location	Survey years
FOFO06I&M	269900	3934000	Forney Creek	Forney Creek, 400 m upstream of the confluence with Huggins Creek	1994
FOFO07I&M	268400	3932970	Forney Creek	Forney Creek, upstream of the confluence with Board Camp Branch	1994
FOFO08I&M	267620	3931210	Forney Creek	Forney Creek, 500 m upstream of the confluence with Bee Gum Branch	1994
FOFO11I&M	267058	3928168	Forney Creek	250 m downstream of the confluence of Bear Creek and Forney Creek, around 270 m downstream of site FOBC01	1994
FOFO12I&M	267337	3927653	Forney Creek	800 m downstream of site FOFO01	1994
FOUN02I&M	272680	3936170	Forney Creek	an unnamed tributary of Forney Creek, 1st order	1994
FOWO10I&M	267580	3929650	Forney Creek	Whiteoak Branch, 200 m upstream of the confluence with Forney Creek	1994
GRGR01I&M	296269	3960065	Greenbrier Creek	Greenbrier Creek	1996
HSBC01I&M	241840	3949800	Hesse Creek	Beard Cane Creek, 1st order	1997
HSBS01I&M	242337	3950185	Hesse Creek	Hesse Creek, 400 m upstream of the confluence with Beard Cane Creek	1997
HSBS02I&M	245940	3947150	Hesse Creek	An unnamed tributary of Hesse Creek, 1st order	1997
HZDF01I&M	257560	3935900	Hazel Creek	Defeat Branch, upstream of the confluence with Roaring Creek	1995-1997, 2001- 2002
HZHZ00I&M	252715	3928915	Hazel Creek	Hazel Creek, 2nd order	1994
HZHZ01I&M	253210	3928620	Hazel Creek	Hazel Creek, 800 m downstream of site HZHZ00	1995-2003
HZHZ02I&M	258690	3931950	Hazel Creek	Hazel Creek, 60 m downstream of the confluence with Cold Spring Branch	1995-2003
HZHZ03I&M	262410	3934830	Hazel Creek	Hazel Creek, above Proctor Creek	1995-2001, 2003
HZLFA1I&M	254250	3932530	Hazel Creek	Little Fork, 300 m upstream of the confluence with Sugar Fork	1995
HZLFB1I&M	254260	3932440	Hazel Creek	Little Fork, 50 m downstream of site HZLFA1	1995

Site ID	coordX	coordY	Watershed	Location	Survey years
ICIC01I&M	294100	3959200	Indian Camp Creek	Indian Camp Creek, 200 m upstream of the confluence with Maddron Creek	1996
ICIC02I&M	294080	3956980	Indian Camp Creek	Indian Camp Creek, far upstream of site ICIC01	1996
LCLC01I&M	273720	3951840	Leconte Creek	LeConte Creek, downstream of the confluence with an unnamed tributary	1995-2003
MLCH01I&M	259131	3942118	Middle Prong Little River	Churn Hollow, above Sams Creek	1996
MLSA01I&M	259130	3942380	Middle Prong Little River	Sams Creek, 320 m downstream of the confluence with Churn Hollow	1993-1996, 1998-1999, 2001-2003
MLSA02I&M	259250	3940490	Middle Prong Little River	Sams Creek	1993-1995, 1998-2000, 2002-2003
MLSA03I&M	259427	3940200	Middle Prong Little River	Sams Creek, 350 m upstream of site MLSA02	2001
MLST01I&M	259070	3940670	Middle Prong Little River	Starkey Creek, 100 m upstream of the confluence with Sams Creek	1993-1996, 1998-1999, 2001-2003
MLST02I&M	258819	3940403	Middle Prong Little River	380 m upstream of site MLST02	1996
MLTH02I&M	257961	3943615	Middle Prong Little River	Thunderhead Prong, 100 m upstream of the confluence with Sams Creek	1996
MPCA01I&M	281560	3950030	Middle Prong Little Pigeon	Cannon Creek	1994, 1996
MPRB01I&M	288717	3953820	Middle Prong Little Pigeon	Ramsay Branch, above Middle Prong Little Pigeon	2001
MPRC01I&M	283795	3954222	Middle Prong Little Pigeon	Rhododendron Creek	2001
MPSP01I&M	282930	3948590	Middle Prong Little Pigeon	Shutts Branch	1994-1995, 2003
OWBF01I&M	285310	3940790	Oconaluftee River	Beech Flats Prong, 700 m upstream of the confluence with Oconaluftee River	1998
OWBF04I&M	281213	3942306	Oconaluftee River	Beech Flats Prong, 4500 m upstream of site OWBF01	1998

Site ID	coordX	coordY	Watershed	Location	Survey years
OWCO01I&M	287662	3937982	Oconaluftee River	Collins Creek	1998
OWKP01I&M	285960	3940660	Oconaluftee River	Kephart Prong, 100 m upstream of the confluence with Oconaluftee River	1998
OWMG01I&M	289092	3932715	Oconaluftee River	Mingus Creek	1998
OWOC01I&M	291359	3935584	Oconaluftee River	Oconaluftee River, 1400 m upstream of the confluence with Couches Creek	1998
OWOC02I&M	288020	3938979	Oconaluftee River	Oconaluftee River, 900 m upstream of the confluence with Collins Creek	1998
PHPC01I&M	274714	3925721	Peachtree Creek	Peachtree Creek	1997
PTPC01I&M	229580	3938550	Panther Creek	Panther Creek	1994
RMRM01I&M	287910	3959450	Ramsey Creek	Ramsey Creek	1996
RRUN01I&M	277120	3951960	Rocky Spur Branch	an unnamed tributary above Rocky Spur Branch	1996
RVBC04I&M	293880	3945440	Raven Fork	Bulldie Creek, upstream of the confluence with Breedlove Branch	1995
RVEC08I&M	295150	3942990	Raven Fork	Enloe Creek, 270 m upstream of the confluence with Raven Fork	1995
RVLf02I&M	294260	3948060	Raven Fork	Left Fork Raven Fork, downstream of the confluence with Raven Fork	1995
RVRf01I&M	296740	3946430	Raven Fork	Right Fork Raven Fork, 1st order	1995
RVRV03I&M	295060	3946630	Raven Fork	Raven Fork, 100 m downstream of the confluence of Left Fork Raven Fork and Right Fork Raven Fork	1995
RVRV05I&M	295160	3944760	Raven Fork	Raven Fork, 3200 m downstream of site RVRV03	1995
RVRV06I&M	296190	3943670	Raven Fork	Raven Fork, 100 m downstream of the confluence with Jones Creek, 2200 m downstream of site RVRV05	1995
RVRV07I&M	295860	3942870	Raven Fork	Raven Fork, 1000 m downstream of site RVRV06	1995
RVRV09I&M	294750	3940520	Raven Fork	Lower end of Raven Fork, at park boundary	1995

Site ID	coordX	coordY	Watershed	Location	Survey years
SASA01I&M	285512	3958276	Soak Ash Creek	Soak Ash Creek	1996
SHSH01I&M	229440	3935840	Shop Creek	Shop Creek	1994
SRSF01I&M	297290	3940050	Straight Fork	Lower end of Straight Fork	1994
SRSF02I&M	299560	3944460	Straight Fork	Straight Fork, 6000 m upstream of site SRSF01	1994
TBTB01I&M	229760	3934720	Tabcat Creek	Tabcat Creek	1994
TWMS01I&M	239470	3929000	Twentymile Creek	Moore Springs Branch, upstream of the confluence with an unnamed tributary	1994- 2003
TWTW02I&M	239665	3928768	Twentymile Creek	Twentymile Creek, 250 m upstream of the confluence with Moore Springs Branch	1996
UTSA11I&M					1996
WLFB01I&M	254173	3947796		Flint Branch, 200 m upstream of the confluence with West Prong Little River	2001
WLPB01I&M	252387	3945236		Pinkroot Branch, 100 m upstream of the confluence with Laurel Creek	2001
WOWO01I&M	251320	3946790			1997
WPAL01I&M	277990	3945460	Walker Camp Prong	Alum Cave Creek, upstream of the confluence with Walker Camp Prong	1993-1994
WPFC01I&M	268661	3951111		Fighting Creek, 300 m upstream of the confluence with Hickory Flats Branch	2001
WPLP01I&M	271530	3953900		Lower end of West Prong Little Pigeon, close to park boundary	1995-1996
WPRP01I&M	276254	3945214		Road Prong	1993-2003
WPWC01I&M	281100	3944730		Walker Camp Prong, below the confluence with an unnamed tributary	2001

Appendix 10. Literature Review of Toxicity Thresholds for Fish and Benthic Macroinvertebrates Related to Stream Acidification

Fish and macroinvertebrate survival, growth and productivity are dependent on both biological and environmental factors. Long-term acid deposition can cause chronic and episodic aquatic acidification, leading to the depression of pH and increase of aluminum and metals. Most studies about the toxicity of stream acidification to salmonids and macroinvertebrates emphasize the effects of reduced pH, elevated aluminum and metals concentration to fish abundance and mortality, and macroinvertebrate biodiversity. Few studies also researched the toxicity threshold of nitrate and nitrite to aquatic biota (Westin 1974, Lewis and Morris 1986). As the stream concentrations of nitrate and nitrite in GRSM are around 100 times lower than the toxicity threshold, the current report will not discuss the toxicity of nitrate and nitrite but just pH, aluminum, and metals.

10.1. pH

Protons (H^+) could be lethal to fish by causing loss of Na^+ and Cl^- across the gills (Spry and Wiener 1991). The mechanism of acid toxicity to fish and macroinvertebrates is to disrupt ion regulation, leading to a severe deficiency of extracellular ions (Courtney and Clements 1998, Felten and Guérol 2006). Generally, the reduction of pH will lead to an increase of aluminum concentrations in stream which increases toxicity. However, the co-existing calcium can prolong survival time of fishes in an acidic solution. Concentrations above 1.4 mg L^{-1} of calcium can bring a marked improvement in fish status even in the most acid lakes, with pH 4.3-4.6 (Howells et al. 1983). Aqueous calcium reduces the toxicity of both H^+ and aluminum at the gills, presumably by reducing gill membrane permeability and subsequent loss of ions (Spry and Wiener 1991).

Alabaster and Lloyd (1980) reported that there is likely a harmful effect to the eggs and fry of salmonids when pH is in the range of 4.5 to 5.0. When pH is reduced to 3.5 to 4.0, it is lethal to salmonids. For macroinvertebrates, acidity may affect diversity, and the abundance of some species sensitive to acid will be significantly reduced. One study about macroinvertebrate communities in 200 streams of the western Adirondack Mountains found that macroinvertebrate assemblages were usually unaffected above pH 6.4, were slightly impacted at pH of 5.7-6.4, moderately impacted from pH of 5.1-5.7, and severely impacted at pH < 5.1 (Baldigo et al. 2009). Table 10.1 summarizes the effects of different pH to different biota and life stage by different experiments.

10.2. Metals

Acute metal toxicity to salmonids is often characterized by gill damage and the hypersecretion of mucus (Handy and Eddy 1990). Mortalities are related to physiological disturbances to respiration resulting in hypoxia and also ionoregulatory disturbances resulting in body ion depletion.

10.2.1 Dissolved Aluminum

Dissolved aluminum is often regarded as the most toxic metal for invertebrates in acidified waters (Hermann et al. 1993). The mechanism of aluminum toxicity to fish is attributed to the inability of fish to maintain their osmoregulatory balance and respiratory problems associated with the coagulation of mucous on the gills (Driscoll 1985, Exley et al. 1991, Hermann et al. 1993). Aluminum tends to accumulate in the gills rather than other organs (Spry and Wiener 1991), where it is presumed to displace Ca^{2+} and cause increased ion efflux and decreases in ion influx, loss of electrolytes, hemo-concentration, and impairment of oxygen delivery to the tissues (Dussault et al. 2004). Except for the precipitation of solid $Al(OH)_3$ or cellular internalization of Al^{3+} , Poléo (1995) proposed that the process of aluminum polymerization is a mechanism of acute toxicity to fish at pH 5.0-6.0. Also, Poléo (1995)

suggested that positively charged Al-hydroxides bind to negatively charged sites of the gill surface to produce an aluminum polymer, leading to severe clogging of the interlamellar space. This physical surface effect leads to acute hypoxia. As a result, the toxicity of aluminum applies primarily to fish at the gill-breathing stages. Therefore, mortality of fish by aluminum is primarily due to asphyxia at pH 6.1 and to electrolyte loss at pH 4.5 (Neville and Campbell 1988).

In contrast to the adverse effect of high levels of aluminum, low levels of aluminum may protect fish from the effects of high hydrogen ion concentration by blocking the membrane permeability of hydrogen ions (Evans et al. 1988, Hermann et al. 1993). Toxicity levels are determined by the forms of dissolved aluminum (Table 10.2), and in general, inorganic monomeric aluminum is most toxic to fish, and the aluminum complexed to organic matter has the least toxicity (Driscoll et al. 1980, Driscoll 1985, Baker et al. 1996).

The toxicity of aluminum is affected by other chemicals, including pH, calcium and DOC, and also by fish stage (Table 10.2). It was reported that aluminum at less than $500 \mu\text{g L}^{-1}$ at pH 4.8-5.2 demonstrated a toxic effect to brook trout but had no effect at higher or lower pH (Schofield and Trojnar 1980). Calcium can moderate the toxicity of aluminum by reducing plasma ion loss (Muniz and Leivestad 1980). At conditions with low pH, low calcium, and high aluminum concentrations, survival may be reduced, growth may be affected and consequently productivity will be low. Aluminum could complex with DOC to be less toxic (Spry and Wiener 1991, Serrano et al. 2008).

The most sensitive stage to acid is the newly hatched fry, but the later swim-up fry is more sensitive to aluminum (Baker and Schofield 1980). The embryo is the life stage least sensitive to aluminum. After hatching, the sensitivity of fish to both acid and aluminum decreases with increasing age - a pattern reported for brook trout (Spry and Wiener 1991). It was suggested that salmonid eggs and yolk sac fry are less vulnerable to the combination of low pH and aluminum than other early life stages (Serrano et al. 2008).

Driscoll et al. (2001) suggested that the appropriate thresholds for chemical and biological recovery in streams and lakes of the northeastern US are pH of 6.0 and Al_{IM} concentration of $2.0 \mu\text{mol L}^{-1}$. The mortality of fish is also determined by the length of time that they are exposed; some studies show that two days of exposure to acutely toxic Al_{IM} concentrations is the approximate minimum exposure before brook trout begin to die (Gagen et al. 1993, Simonin et al. 1993, Van Sickle et al. 1996, Baldigo and Murdoch 1997). Some other aluminum thresholds were reported in the northeastern US: significant mortality of brook trout was found when Al_{IM} levels exceeded 0.2 mg L^{-1} for two or more days (Baldigo and Murdoch 1997), or when Al_{TOT} concentration reached $0.2 - 0.3 \text{ mg L}^{-1}$ for 1.5 or more days (Gagen and Sharpe 1987a, 1987b), or when Al_{M} concentration reached 0.1 mg L^{-1} during acid episodes (Simonin et al. 1993), or when Al_{IM} and/or Al_{TOT} exceeded either 0.2 or 0.3 mg L^{-1} under low Ca ($< 2.0 \text{ mg L}^{-1}$), DOC ($< 2.0 \text{ mg L}^{-1}$) and pH (4.4 - 5.2) conditions (Van Sickle et al. 1996).

10.2.2 Other Dissolved Metals

Many dissolved metals, especially select heavy metals, have been studied regarding toxicity to aquatic biota; however, in GRSM, only five metals in streams were monitored (Al, Cu, Fe, Mn, and Zn). The review of toxicity threshold values will focus on these five metals (Table 10.3).

Table 10.1. Toxicity threshold values of pH for trout (salmonids) and benthic macroinvertebrates.

Biota name	Methods	pH	Co-existing chemicals	Effects	References
Fish		4.5	$\text{Ca}^{2+} < 0.8 \text{ mg L}^{-1}$	Lakes will be fishless	Howells et al. 1983
Brook trout	Laboratory exposures for 5 months	5.5		Reduced growth	Menendez 1976
Brook trout	Field experiments in acid stream water	~5		Reduced growth	Muniz and Leivestad 1979
Brook trout fry	Field exposure to episodic acidification for 20 days in Adirondack lake	4.8		100% mortality	Van Offelen et al. 1994
Brook trout, eggs, larvae and young	Lab exposure for 30 days	4.5	$\text{Al} = 300 \mu\text{g L}^{-1}$	Adverse effects on mortality, growth, behavior and biochemical responses	Cleveland et al. 1986
		5.5			
Brook trout	Field exposure to episodic acidification	< 5.0-5.2	Inorganic $\text{Al} > 100 -200 \mu\text{g L}^{-1}$	Trout abundance was reduced	Baker et al. 1996
Introduced brook trout, sac fry	In-situ experiment within the North Branch of the Moose River	4.32-4.4	$\text{Al}_{\text{im}} = 0.19-0.21 \text{ mg L}^{-1}$ $\text{Ca}^{2+} = 1.13-1.40 \text{ mg L}^{-1}$ $\text{DOC} = 6.0-6.9 \text{ mg L}^{-1}$	0% survival after 240 hours	Johnson et al. 1987
Introduced brook trout, feeding fry		4.53~4.87	$\text{Al}_{\text{im}} = 0.18-0.25 \text{ mg L}^{-1}$ $\text{Ca}^{2+} = 1.08-1.68 \text{ mg L}^{-1}$ $\text{DOC} = 3.8-6.4 \text{ mg L}^{-1}$	0% survival after 336 hours	
Introduced brook trout, young of the year		4.37~4.68	$\text{Al}_{\text{im}} = 0.11-0.34 \text{ mg L}^{-1}$ $\text{Ca}^{2+} = 0.41-1.30 \text{ mg L}^{-1}$ $\text{DOC} = 7.3-9.0 \text{ mg L}^{-1}$	0% survival after 1920 hours	
Introduced brook trout, yearling		4.44~4.68	$\text{Al}_{\text{im}} = 0.11-0.18 \text{ mg L}^{-1}$ $\text{Ca}^{2+} = 0.41-1.03 \text{ mg L}^{-1}$ $\text{DOC} = 8.0-9.0 \text{ mg L}^{-1}$	0% survival after 672 hours	
Rainbow trout	Lab exposure up to 8 weeks	5.2	$\text{Ca}^{2+} = 12 \pm 7 \mu\text{mol L}^{-1}$	decreased swimming capacity by 5%	Dussault et al. 2004
Juvenile rainbow trout	Lab exposure to synthesize solution for 36	5.2	$\text{Ca}^{2+} = 28 \mu\text{eq L}^{-1}$	9-16% reduction of swimming capacity	Wilson et al. 1994

Biota name	Methods	pH	Co-existing chemicals	Effects	References
	days				
Rainbow trout	Laboratory exposures to sub-lethal acid conditions over 3.5 months	5.5		Reduced growth	Edwards and Hjeldnes 1977
<i>G. fossarum</i> (Amphipoda), <i>H. pellucidula</i> (Trichoptera), <i>D. cephalotes</i> (Plecoptera)	Exposure for 24, 72 and 120 h in a stream in France	4.73 ± 0.08	Al _{tot} = 28.4 ± 1 µmol L ⁻¹ Ca ²⁺ = 39.1 ± 0.6 µmol L ⁻¹	Decrease in survival rate and Na ⁺ , Cl ⁻ . <i>G. fossarum</i> most sensitive than <i>H. pellucidula</i> and <i>D. cephalotes</i>	Felten and Guérolde 2006
Benthic macroinvertebrates	Exposure to a stream with artificially added HNO ₃ to control pH 4.0, 5.5, 6.5 and 7.4 for 7 days	4.0		Significant fewer individuals and taxa. Reduced abundance resulted primarily from reduced abundance of mayflies (Ephemeroptera)	Courtney and Clements 1998
Benthic macroinvertebrates	Native macroinvertebrate in streams affected by episodic acidification in Swiss streams	< 5.0	Al _{tot} up to 140 µg L ⁻¹	Lower taxonomic richness; scarce empididae, <i>Isoperla rivulorum</i> , <i>Rhithrogena</i> spp. and <i>Baetis</i> spp.	Lepori et al. 2003
Benthic macroinvertebrate	Native macroinvertebrate affected by episodic acidification in British streams	< 5.7-6		<i>Baetis muticus</i> , <i>Heptagenia lateralis</i> and <i>R. semicolorata</i> absent	Kowalik et al. 2007
<i>Baetis alpinus</i> (Ephemeroptera)	Native <i>B. alpinus</i> affected by episodic acidification	4.5-5.6		Decline to 10-20% during acid episodes	Lepori and Ormerod 2005

Table 10.2. Toxicity threshold values of dissolved aluminum concentrations for trout (salmonids).

Fish name	Methods	Al concentrations		Co-existing chemicals	Effects	References
		Total Al	Inorganic monomeric Al			
Brown trout		7 $\mu\text{mol L}^{-1}$		pH = 5.0	Loss of Na and Cl from the blood	Muniz and Leivestad 1979
Brook trout fry	Lab exposure to synthesized solutions for 14 days	18-36 $\mu\text{mol L}^{-1}$		pH = 4.8	Gill damage	Schofield and Trojnar 1980
Brook trout	Lab exposure for 193 days		47 $\mu\text{g L}^{-1}$	pH = 5.0 Ca^{2+} = 0.5 mg L^{-1}	44% mortality	Mount et al. 1988
Brook trout, young of the year	Exposure to stream waters for 30 days during each spring from 1995 to 2000		Median: 4.48 $\mu\text{mol L}^{-1}$; Range: 2.02-13.89	Median: pH = 5.03; NO_3^- = 263 $\mu\text{mol L}^{-1}$	100% mortality	Baldigo et al. 2005
Brook trout	Field exposure to episodic acidification for 10 days	> 200 $\mu\text{g L}^{-1}$		pH < 5.1	10-19% loss of whole-body sodium	Neff et al. 2009
Brook trout, young of the year	Exposure to spring episodic acidification for 30 days in the SW Adirondack Mountains (2001- 2003).		> 4 $\mu\text{mol L}^{-1}$		50-100% mortality during two to four days of exposure	Baldigo and Lawrence 2007
Brook trout, larvae and post-larvae	Lab exposure to softened and dechlorinated water for 13 to 14 days	0.2 mg L^{-1}		pH range from 4.2 to 5.6	Measurable reductions in survival and growth	Baker and Schofield 1982
Adult rainbow trout	Lab exposure to synthesized solutions for 10 days	>10 $\mu\text{mol L}^{-1}$		Pathological changes were more severe with aluminum at pH 5.4 than at pH 4.7	Caused chloride cell necrosis and a decline in cell numbers	Evans et al. 1988

Fish name	Methods	Al concentration		Co-existing chemicals	Effects	References
		Total Al	Inorganic monomeric Al			
Juvenile rainbow trout	26 h of exposure to dechlorinated tap water with added aluminum	> 200 µg/L		pH = 6.0	Affected cough rate, which is defined as disruptions in the ventilation pattern.	Ogilvie and Stechey 1983
Juvenile rainbow trout	26 h of exposure to dechlorinated tap water with added aluminum	> 500 µg L ⁻¹		pH = 6.0	Affected ventilation rate, which is the number of opercular cycles per unit of time.	Ogilvie and Stechey 1983
Rainbow trout	Lab exposure up to 8 weeks	89 µg L ⁻¹		pH = 5.1-5.2 Ca ²⁺ = 12± 7 µmol L ⁻¹	25% survival, decreased swimming capacity by 21%	Dussault et al. 2004
Juvenile rainbow trout	Lab exposure to synthesize solution for 36 days	38 µg L ⁻¹		pH = 5.2 Ca ²⁺ = 28 µeq L ⁻¹	15-21% reduction of swimming capacity	Wilson et al. 1994
Juvenile rainbow trout	Lab exposure to different pH levels with same Al concentration solution for 11 days	2.8 µmol L ⁻¹		pH = 6.1	Uptake of O ₂ across the gill epithelium was reduced	Neville and Campbell 1988
				pH = 4.5	Increased gill membrane permeability to H ⁺ , Na ⁺ and Cl ⁻ ions	
Rainbow trout, fingerlings	Exposure to synthesized solution with varied Al and pH (7.0-9.0) for 45 days	5.2 mg L ⁻¹		pH range from 7.0 to 9.0	Seriously disturbs natural populations of young trout with longer than 6 weeks exposure	Freeman and Everhart 1971

Table 10.3. Toxicity threshold values of metals other than aluminum to fish and macroinvertebrates.

Taxon	Methods	Metals	Co-existing chemicals and conditions	Effects	References
Rainbow trout, swim-up stage	Laboratory exposures to synthesized well water with designed metal concentration	Cd = 1.9 $\mu\text{g L}^{-1}$ Cu = 40 $\mu\text{g L}^{-1}$ Zn = 219 $\mu\text{g L}^{-1}$	pH = 8.24 Alk = 92 mg L^{-1} Hardness = 103 mg L^{-1} as CaCO_3 Ca^{2+} = 25 mg L^{-1} Mg^{2+} = 8.0 mg L^{-1} Na^{+} = 8.3 mg L^{-1} SO_4^{2-} = 18 mg L^{-1} Cl^{-} = 9 mg L^{-1} DOC < 1 mg L^{-1}	Start to affect survival	Besser et al. 2007
Rainbow trout		Zn = 47 $\mu\text{g L}^{-1}$	112 mg L^{-1} CaCO_3 pH = 7.6	Fish avoidance	Black and Birge 1980
Rainbow trout		Zn = 144 $\mu\text{g L}^{-1}$	25 mg L^{-1} CaCO_3 pH = 7.6	Effect on fish ventilation	Cairns et al. 1982
Benthic macroinvertebrate	Exposure to a mixture of Cd, Cu and Zn for 7 days in a stream microcosm	Cd = 1.1 $\mu\text{g L}^{-1}$, Cu = 12 $\mu\text{g L}^{-1}$, Zn = 110 $\mu\text{g L}^{-1}$		Abundance of three mayfly species was reduced by more than 50%	Clements and Kiffney 1994

Toxicity Literature

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Appendix 11. Time Trend Analysis for Brook Trout and Rainbow Trout Metrics Using Linear Regression Analysis to Julian Date.

(Only trends with significant values $p < 0.1$ were reported)

Site ID	Brook Trout							Rainbow Trout						
	N	YOY Density	ADT Density	YOY Biomass	ADT Biomass	YOY K	ADT K	N	YOY Density	ADT Density	YOY Biomass	ADT Biomass	YOY K	ADT K
ABC-4								10	-0.0014	-0.0004	-0.0010	-0.0015		
ACB-2	1							2						
ACB-3	5							2						
ACB-4	5		0.0057					1						
ACB-5	1							1						
ACB-6	1							1						
ADB-1	9							3						
ALC-2	3							1						
ALC-3	2													
BEC-2	16	0.0014	0.0018	0.0004	0.0036			16	-0.0009	-0.0016		-0.0049		0.0000
BEF-2	8				-0.0043			8						
BGP-1	1							1						
BGP-2	1													
BIB-1								2						
BLK-1	1							13		-0.0008		-0.0025		
BLK-2	1							13	-0.0010	-0.0014		-0.0047		
BLK-3								11		-0.0017				
BRC-0								1						
BRC-1C								1						
BRC-33	2							2						
BRC-9	1							1						
BUN-3	20		0.0028		0.0034	0.0000								
CAN-1M								1						
CAN-2								8						
CAN-3M								1						
CHC-1	3													
COK-1	4							4						
COS-1	17							17						

[illegible]

[illegible]

Site ID	Brook Trout							Rainbow Trout						
	YOY	ADT	YOY	ADT	YOY	ADT		YOY	ADT	YOY	ADT	YOY	ADT	
	N	Density	Density	Biomass	Biomass	K		N	Density	Density	Biomass	Biomass	K	
LEC-20	1													
LEC-21	1													
LEC-22	1													
LEC-23	1													
LEC-24	8						0.0000							
LEC-25	1													
LEC-3	2							1						
LEC-4	1													
LEC-5	2							1						
LEC-6	1													
LEC-7	1													
LEC-8	1													
LEC-9	4				0.0040									
LECT-2	5							3						
LJC-1	1							1						
LOB-1	16	0.0004			0.0011	0.0000		2						
LOB-10	7	0.0036			0.0090			5		-0.0012		-0.0048		
LOB-11	8	0.0042			0.0095			6	-0.0006	-0.0010	-0.0001	-0.0048		
LOB-12	8	0.0030			0.0070			4						
LOB-13	8	0.0031			0.0069			4						
LOB-14	7	0.0054			0.0103	-0.0001		4		-0.0026		-0.0096		
LOB-15	7	0.0047			0.0088			4		-0.0017		-0.0054		
LOB-16	7						-0.0001	4		-0.0024				
LOB-17	7							4						
LOB-18	7							4						
LOB-19	8	0.0060			0.0142			3						
LOB-2	16						0.0000	3						
LOB-20	8							5		-0.0027		-0.0101		
LOB-21	8				0.0053			3						
LOB-22	7							2						
LOB-23	7						-0.0001	3						
LOB-25	7				0.0078			2						
LOB-26	7							2						

[illegible]

Site ID	Brook Trout							Rainbow Trout						
	N	YOY Density	ADT Density	YOY Biomass	ADT Biomass	YOY K	ADT K	N	YOY Density	ADT Density	YOY Biomass	ADT Biomass	YOY K	ADT K
MEG-3	4													
MPLP-0								1						
MPLP-1								2						
MPLP-2								1						
MPLP-4								1						
NWP-3								8						0.0000
OCO-3	1							1						
PAL-1	2							3						
PAR-1								2						
PLK-1	1													
PLK-10	2													
PLK-11	1													
PLK-12	1													
PLK-13	1													
PLK-14	1													
PLK-15	1													
PLK-2	1													
PLK-3	2							1						
PLK-4	1													
PLK-5	1													
PLK-6	1													
PLK-7	1													
PLK-8	1													
PLK-9	1													
PTH-1	4							4				0.0108		
PTH-2	4							4						
RFC-1	1							11						
RFC-1N								1						
RFC-2	1							10						
ROC-1	6							6						
ROC-3	4							3						
ROC-5	3							3						
ROC-6	19					0.0000	0.0000	5						

Site ID	Brook Trout							Rainbow Trout						
	N	YOY Density	ADT Density	YOY Biomass	ADT Biomass	YOY K	ADT K	N	YOY Density	ADT Density	YOY Biomass	ADT Biomass	YOY K	ADT K
RPR-1	2							3						
RPR-2	17			0.0001	0.0007		0.0000	17		-0.0007		-0.0026		
SAM-1M								3						
SAM-2								5		-0.0050				
SAM-2M								3						
SAM-3	8		0.0008		0.0028			11		-0.0015				
SAM-3M	1							3						
SAM-4	1							3						
SAM-5	13	0.0016		0.0004	0.0026			10						
SAM-5M	1							3						
SAM-7	2													
SAM-8	2													
SAM-C1								7	0.0059					
SAM-C2								8						
SAM-C3	2							8		0.0032		0.0144		0.0000
SAM-S18								2						
SAM-S19								2						
SAM-S25	1							1						
SAM-S26								1						
SAM-S33	1							1						
SAM-S39	1							1						
SAM-S5	2							2						
SAM-S6								1						
SIL-10	13													
SIL-2	1													
SIL-3	1													
SIL-4	5							4		0.0028				0.0001
SIL-5								1						
SIL-6	4													
SIL-7	1													
SIL-8	1													
SIL-9	14													
STK-2	2							1						

Site ID	Brook Trout							Rainbow Trout						
	N	YOY Density	ADT Density	YOY Biomass	ADT Biomass	YOY K	ADT K	N	YOY Density	ADT Density	YOY Biomass	ADT Biomass	YOY K	ADT K
STK-3	2													
STR-1	5							10						0.0000
TAY-1	12	0.0006	0.0007			0.0000								
TAY-10	1													
TAY-11	12		0.0010		0.0024									
TAY-3	1													
TAY-4	13		0.0010				0.0000							
TAY-5	1													
TAY-6	1													
TAY-7	1													
TAY-8	1													
TAY-9	12		0.0016		0.0036									
TOM-1	1													
TOM-2	1													
TWC-1								1						
WAL-1	1							1						
WAL-2	1													
WCP-1	13							14					0.0001	
WCP-2	14		-0.0010		-0.0031			14	0.0004			0.0013	0.0000	
WIN-1	3							5			-0.0001			
WIN-2	4		0.0026					2						
WIN-3	4		0.0039					2						
WIN-4	4							2						
WPLP-0	1							1						

Appendix 12. Correlation Coefficients and Significant Levels between Biotic Metrics and Chemistry by Using Kendall's Tau Correlation Analysis.

Significant correlation at p-value below 0.05 in bold.

		pH	ANC	Cond	Cl	NO3	SO4	Na	NH4	K	Mg	Ca	BCS	Al*	Al	Cu	Fe	Mn	Si	Zn
BKT YOY_Den	τ	-0.08	-0.03	-0.11	0.02	0.15	-0.15	0.04	0.04	0.11	-0.06	-0.08	-0.07	0.00	-0.31	0.09	0.05	0.10	0.02	-0.06
	p	0.09	0.51	0.02	0.71	0.00	0.00	0.41	0.44	0.03	0.23	0.10	0.16	0.99	0.00	0.43	0.67	0.34	0.88	0.59
	N	195	194	195	195	195	195	194	195	195	195	195	194	194	41	41	41	41	41	40
BKT YOY_Biom	τ	-0.02	0.02	-0.14	0.00	0.11	-0.19	0.08	0.06	0.12	-0.05	-0.10	0.00	-0.07	-0.32	0.06	0.03	0.05	0.08	-0.01
	p	0.68	0.69	0.00	0.98	0.03	0.00	0.10	0.31	0.02	0.29	0.04	0.92	0.21	0.00	0.61	0.75	0.66	0.47	0.94
	N	195	194	195	195	195	195	194	195	195	195	195	194	194	41	41	41	41	41	40
BKT YOY_K	τ	-0.03	-0.11	0.17	-0.12	0.15	0.16	-0.06	-0.05	-0.04	0.12	0.08	-0.11	0.15	0.12	-0.14	0.12	0.14	-0.22	-0.07
	p	0.52	0.03	0.00	0.02	0.00	0.00	0.24	0.41	0.43	0.02	0.10	0.03	0.00	0.31	0.23	0.28	0.24	0.06	0.53
	N	174	173	174	174	174	174	173	174	174	174	174	173	173	37	37	37	37	37	36
BKT ADT_Den	τ	-0.15	-0.20	-0.03	0.17	0.30	-0.04	-0.16	0.12	-0.05	-0.05	-0.02	-0.24	0.06	-0.23	0.11	0.21	0.15	-0.23	-0.03
	p	0.00	0.00	0.51	0.00	0.00	0.48	0.00	0.04	0.32	0.34	0.68	0.00	0.31	0.03	0.30	0.05	0.17	0.03	0.75
	N	163	162	163	163	163	163	162	163	163	163	163	162	162	42	42	42	42	42	41
BKT ADT_Biom	τ	-0.16	-0.20	0.00	0.15	0.35	-0.01	-0.21	0.16	-0.12	0.01	0.03	-0.21	0.03	-0.19	0.12	0.22	0.14	-0.30	0.01
	p	0.00	0.00	0.93	0.00	0.00	0.87	0.00	0.00	0.02	0.84	0.54	0.00	0.64	0.07	0.25	0.04	0.19	0.01	0.95
	N	163	162	163	163	163	163	162	163	163	163	163	162	162	42	42	42	42	42	41
BKT ADT_K	τ	-0.04	-0.09	0.16	-0.03	0.20	0.12	-0.02	0.01	-0.09	0.15	0.04	-0.11	0.06	-0.04	0.06	0.11	0.12	-0.27	0.06
	p	0.49	0.11	0.00	0.52	0.00	0.02	0.74	0.87	0.10	0.01	0.47	0.04	0.28	0.74	0.58	0.32	0.28	0.01	0.57
	N	159	158	159	159	159	159	158	159	159	159	159	158	158	42	42	42	42	42	41
RBT YOY_Den	τ	0.15	0.27	0.08	0.05	-0.14	-0.15	0.24	0.03	0.25	0.15	0.13	0.27	-0.27	-0.46	-0.26	-0.05	-0.46	0.30	-0.36
	p	0.00	0.00	0.14	0.38	0.01	0.00	0.00	0.61	0.00	0.01	0.01	0.00	0.00	0.01	0.11	0.75	0.01	0.07	0.03
	N	164	161	163	164	164	164	162	162	163	163	162	161	161	20	20	19	20	20	20
RBT YOY_Biom	τ	0.23	0.35	0.17	0.09	-0.15	-0.14	0.32	0.02	0.30	0.21	0.17	0.34	-0.33	-0.33	-0.31	-0.13	-0.50	0.41	-0.28
	p	0.00	0.00	0.00	0.10	0.00	0.01	0.00	0.70	0.00	0.00	0.00	0.00	0.00	0.04	0.06	0.46	0.00	0.01	0.09
	N	163	160	162	163	163	163	161	161	162	162	161	160	160	20	20	19	20	20	20
RBT YOY_K	τ	0.05	0.12	0.00	-0.13	-0.09	-0.13	0.04	-0.01	-0.02	0.07	0.03	0.11	-0.05	-0.16	-0.11	0.15	-0.05	-0.15	-0.30
	p	0.41	0.03	0.99	0.02	0.13	0.02	0.44	0.87	0.73	0.25	0.61	0.05	0.40	0.36	0.54	0.42	0.77	0.41	0.09
	N	141	138	140	141	141	141	139	139	140	140	139	138	138	17	17	16	17	17	17

		pH	ANC	Cond	Cl	NO3	SO4	Na	NH4	K	Mg	Ca	BCS	Al*	Al	Cu	Fe	Mn	Si	Zn
RBT ADT_Den	τ	0.15	0.16	-0.04	0.06	-0.20	-0.20	0.06	0.04	0.20	0.01	0.04	0.16	-0.10	0.22	0.05	-0.12	0.06	0.17	-0.13
	p	0.01	0.01	0.50	0.29	0.00	0.00	0.33	0.51	0.00	0.82	0.50	0.01	0.15	0.17	0.77	0.48	0.70	0.30	0.44
	N	133	132	133	133	133	133	132	133	133	133	133	132	132	20	20	20	20	20	20
RBT ADT_Biom	τ	0.25	0.26	0.09	0.07	-0.21	-0.13	0.09	0.04	0.27	0.11	0.14	0.25	-0.13	0.42	0.20	-0.15	0.05	0.22	0.05
	p	0.00	0.00	0.12	0.26	0.00	0.03	0.12	0.56	0.00	0.05	0.02	0.00	0.06	0.01	0.23	0.36	0.75	0.17	0.75
	N	133	132	133	133	133	133	132	133	133	133	133	132	132	20	20	20	20	20	20
RBT ADT_K	τ	-0.06	-0.08	0.05	-0.05	0.18	0.07	0.09	-0.13	-0.08	0.02	-0.07	-0.07	0.10	0.05	-0.18	0.02	-0.06	0.05	0.11
	p	0.28	0.20	0.43	0.41	0.00	0.25	0.11	0.04	0.19	0.74	0.25	0.25	0.15	0.75	0.28	0.90	0.72	0.75	0.52
	N	133	132	133	133	133	133	132	133	133	133	133	132	132	20	20	20	20	20	20
NCBI	τ	0.01	0.02	0.24	-0.06	0.03	0.18	0.02	0.01	-0.03	0.22	0.20	0.05	0.00						
	p	0.88	0.77	0.00	0.27	0.65	0.00	0.71	0.94	0.57	0.00	0.00	0.34	0.96						
	N	141	141	140	141	141	140	141	141	140	141	141	141	141						
EPTR	τ	0.21	0.24	-0.16	0.02	-0.15	-0.16	0.13	-0.02	0.26	-0.09	-0.04	0.21	-0.22						
	p	0.00	0.00	0.01	0.76	0.01	0.01	0.02	0.80	0.00	0.12	0.53	0.00	0.00						
	N	141	141	140	141	141	140	141	141	140	141	141	141	141						
EPTA	τ	-0.07	-0.15	0.05	-0.02	0.13	0.09	-0.14	-0.10	-0.07	0.01	-0.01	-0.13	0.12						
	p	0.23	0.01	0.36	0.76	0.03	0.11	0.01	0.12	0.23	0.87	0.89	0.03	0.06						
	N	141	141	140	141	141	140	141	141	140	141	141	141	141						
BIOC	τ	0.13	0.16	-0.08	0.03	-0.08	-0.05	0.10	-0.04	0.19	0.00	0.10	0.17	-0.16						
	p	0.07	0.02	0.29	0.64	0.24	0.53	0.17	0.63	0.01	0.99	0.17	0.02	0.04						
	N	133	133	132	133	133	132	133	133	132	133	133	133	133						
TR	τ	0.23	0.32	-0.17	0.02	-0.17	-0.23	0.22	0.08	0.27	-0.07	-0.02	0.27	-0.26						
	p	0.00	0.00	0.00	0.77	0.00	0.00	0.00	0.24	0.00	0.25	0.70	0.00	0.00						
	N	141	141	140	141	141	140	141	141	140	141	141	141	141						
TA	τ	0.22	0.27	-0.11	-0.07	-0.09	-0.19	0.17	0.06	0.25	0.01	0.10	0.32	-0.28						
	p	0.00	0.00	0.05	0.22	0.10	0.00	0.00	0.38	0.00	0.82	0.07	0.00	0.00						
	N	141	141	140	141	141	140	141	141	140	141	141	141	141						
RCFI	τ	0.24	0.26	-0.12	0.01	-0.21	-0.07	0.15	0.01	0.17	0.00	0.08	0.29	-0.29						
	p	0.00	0.00	0.05	0.85	0.00	0.27	0.01	0.84	0.00	0.96	0.18	0.00	0.00						
	N	141	141	140	141	141	140	141	141	140	141	141	141	141						
RCGA	τ	0.19	0.33	-0.14	0.08	-0.16	-0.28	0.31	0.15	0.34	-0.08	-0.05	0.28	-0.28						
	p	0.00	0.00	0.02	0.16	0.01	0.00	0.00	0.03	0.00	0.15	0.44	0.00	0.00						

		pH	ANC	Cond	Cl	NO3	SO4	Na	NH4	K	Mg	Ca	BCS	Al*	Al	Cu	Fe	Mn	Si	Zn
	N	141	141	140	141	141	140	141	141	140	141	141	141	141						
RPRE	τ	0.07	0.15	-0.11	0.02	-0.09	-0.12	0.06	0.04	0.15	-0.11	-0.04	0.09	-0.09						
	p	0.22	0.01	0.07	0.71	0.11	0.04	0.27	0.56	0.01	0.06	0.49	0.11	0.13						
	N	141	141	140	141	141	140	141	141	140	141	141	141	141						
RSCR	τ	0.33	0.36	-0.19	-0.04	-0.21	-0.24	0.20	0.00	0.23	-0.04	0.00	0.35	-0.35						
	p	0.00	0.00	0.00	0.47	0.00	0.00	0.00	1.00	0.00	0.46	1.00	0.00	0.00						
	N	141	141	140	141	141	140	141	141	140	141	141	141	141						
RSHR	τ	0.25	0.25	-0.16	-0.05	-0.08	-0.22	0.19	-0.02	0.22	-0.06	-0.04	0.20	-0.21						
	p	0.00	0.00	0.01	0.46	0.20	0.00	0.00	0.81	0.00	0.31	0.56	0.00	0.00						
	N	141	141	140	141	141	140	141	141	140	141	141	141	141						
ACFI	τ	0.09	0.07	-0.14	0.04	-0.18	0.00	0.06	0.02	0.05	-0.02	0.02	0.10	-0.08						
	p	0.11	0.21	0.02	0.45	0.00	0.96	0.32	0.77	0.40	0.79	0.67	0.09	0.18						
	N	141	141	140	141	141	140	141	141	140	141	141	141	141						
ACGA	τ	-0.05	-0.01	0.05	0.04	0.12	-0.07	0.02	0.10	0.08	0.02	0.01	0.02	0.00						
	p	0.42	0.91	0.39	0.49	0.03	0.21	0.68	0.14	0.17	0.77	0.87	0.79	0.95						
	N	140	140	139	140	140	139	140	140	139	140	140	140	140						
APRE	τ	-0.06	-0.01	-0.03	0.03	-0.03	-0.04	0.03	-0.04	-0.02	-0.12	-0.16	-0.10	0.07						
	p	0.29	0.86	0.57	0.63	0.56	0.46	0.59	0.51	0.76	0.03	0.00	0.07	0.27						
	N	141	141	140	141	141	140	141	141	140	141	141	141	141						
ASCR	τ	0.23	0.19	-0.02	-0.10	-0.12	-0.02	0.05	-0.11	0.04	0.02	0.10	0.21	-0.22						
	p	0.00	0.00	0.77	0.08	0.04	0.73	0.40	0.09	0.50	0.68	0.09	0.00	0.00						
	N	141	141	140	141	141	140	141	141	140	141	141	141	141						
ASHR	τ	-0.09	-0.12	0.08	-0.09	0.10	0.09	-0.14	-0.03	-0.18	0.07	0.05	-0.11	0.11						
	p	0.14	0.04	0.15	0.13	0.08	0.12	0.01	0.64	0.00	0.19	0.42	0.05	0.08						
	N	141	141	140	141	141	140	141	141	140	141	141	141	141						

τ : Kendall's tau correlation coefficient

P: p-value

N: number of observation

Appendix 13. Correlation Coefficients and Significant Levels between Trout and Macroinvertebrates Metrics by Using Kendall's Tau Correlation Analysis.

Significant correlation at p-value below 0.05 in bold.

		NCBI	EPTR	EPTA	BIOC	TR	TA	RCFI	RCGA	RPRE	RSCR	RSHR	ACFI	ACGA	APRE	ASCR	ASHR
BKT	τ	-0.23	0.05	-0.05	0.03	0.10	0.10	0.00	0.09	-0.01	0.05	0.23	0.02	0.05	0.13	-0.08	-0.10
YOY_ Den	p-value	0.00	0.42	0.42	0.69	0.13	0.13	0.99	0.17	0.93	0.51	0.00	0.73	0.44	0.05	0.20	0.12
	N	109	109	109	106	109	109	109	109	109	109	109	109	108	109	109	109
BKT	τ	-0.19	0.03	-0.08	0.02	0.11	0.09	0.02	0.09	-0.02	0.05	0.23	0.06	0.01	0.13	-0.10	-0.08
YOY_ Biom	p-value	0.00	0.61	0.23	0.84	0.10	0.16	0.75	0.18	0.82	0.47	0.00	0.33	0.86	0.05	0.13	0.22
	N	110	110	110	107	110	110	110	110	110	110	110	110	109	110	110	110
BKT	τ	-0.02	-0.02	0.00	0.04	-0.01	-0.01	-0.06	0.02	0.00	-0.01	-0.10	-0.06	0.13	-0.12	-0.08	-0.05
YOY_K	p-value	0.82	0.82	0.99	0.61	0.94	0.93	0.42	0.79	0.98	0.88	0.17	0.35	0.05	0.08	0.25	0.47
	N	98	98	98	95	98	98	98	98	98	98	98	98	97	98	98	98
BKT	τ	-0.22	-0.02	0.12	-0.08	0.01	0.07	-0.06	0.05	0.00	-0.03	0.13	-0.08	0.12	0.04	-0.06	0.03
ADT_ Den	p-value	0.00	0.73	0.06	0.31	0.85	0.26	0.34	0.43	0.99	0.69	0.05	0.19	0.06	0.53	0.37	0.62
	N	112	112	112	109	112	112	112	112	112	112	112	112	111	112	112	112
BKT	τ	-0.24	-0.03	0.10	-0.05	0.00	0.08	-0.06	0.04	-0.02	-0.04	0.12	-0.10	0.12	0.05	-0.03	0.03
ADT_ Biom	p-value	0.00	0.67	0.10	0.50	0.96	0.20	0.35	0.50	0.81	0.55	0.08	0.11	0.05	0.45	0.65	0.62
	N	112	112	112	109	112	112	112	112	112	112	112	112	111	112	112	112
BKT	τ	0.08	-0.10	0.02	-0.07	-0.05	-0.01	-0.18	0.00	-0.10	-0.01	-0.03	-0.09	0.09	-0.06	-0.15	-0.01
Adult_K	p-value	0.22	0.13	0.75	0.40	0.49	0.90	0.01	0.96	0.13	0.88	0.64	0.15	0.18	0.40	0.03	0.85
	N	108	108	108	105	108	108	108	108	108	108	108	108	107	108	108	108
RBT	τ	0.19	0.19	-0.24	0.16	0.32	0.09	0.29	0.27	0.10	0.21	0.28	0.10	-0.11	-0.08	0.31	0.01
YOY_ Den	p-value	0.07	0.10	0.03	0.22	0.00	0.39	0.01	0.02	0.35	0.06	0.02	0.34	0.32	0.48	0.00	0.93
	N	44	44	44	42	44	44	44	44	44	44	44	44	44	44	44	44
RBT	τ	0.24	0.21	-0.26	0.19	0.34	0.12	0.31	0.32	0.10	0.23	0.29	0.10	-0.06	-0.10	0.30	-0.02
YOY_ Biom	p-value	0.03	0.06	0.02	0.14	0.00	0.27	0.01	0.00	0.35	0.05	0.01	0.36	0.59	0.38	0.01	0.84
	N	44	44	44	42	44	44	44	44	44	44	44	44	44	44	44	44
RBT	τ	0.14	0.07	0.09	0.10	0.15	0.23	0.09	0.28	-0.23	-0.03	0.01	-0.15	0.17	0.00	0.11	-0.05
YOY_K	p-value	0.31	0.63	0.52	0.56	0.28	0.10	0.51	0.05	0.10	0.82	0.95	0.29	0.22	0.98	0.42	0.69
	N	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27

		NCBI	EPTR	EPTA	BIOC	TR	TA	RCFI	RCGA	RPRE	RSCR	RSHR	ACFI	ACGA	APRE	ASCR	ASHR
RBT	τ	0.10	0.25	-0.13	0.28	0.32	0.18	0.32	0.30	0.15	0.13	0.26	0.23	0.03	-0.21	0.25	-0.14
ADT_ Den	p-value	0.34	0.02	0.22	0.03	0.00	0.09	0.00	0.01	0.15	0.24	0.02	0.03	0.75	0.04	0.02	0.18
	N	44	44	44	42	44	44	44	44	44	44	44	44	44	44	44	44
RBT	τ	0.04	0.21	-0.14	0.29	0.30	0.18	0.37	0.32	0.10	0.12	0.19	0.24	0.03	-0.27	0.26	-0.11
ADT_ Biom	p-value	0.67	0.05	0.17	0.03	0.00	0.09	0.00	0.00	0.36	0.26	0.08	0.02	0.75	0.01	0.01	0.28
	N	44	44	44	42	44	44	44	44	44	44	44	44	44	44	44	44
RBT	τ	-0.15	-0.01	0.00	-0.18	-0.03	-0.05	0.05	-0.01	0.03	0.02	-0.10	0.02	0.14	0.09	0.03	-0.20
Adult_K	p-value	0.15	0.93	0.97	0.16	0.81	0.61	0.67	0.95	0.75	0.87	0.37	0.86	0.18	0.37	0.79	0.05
	N	44	44	44	42	44	44	44	44	44	44	44	44	44	44	44	44

Appendix 14. Correlation Coefficients and Significant Levels between Brook Trout and Rainbow Trout by Kendall's Tau Correlation Analysis.

Significant correlation ($p < 0.05$) in bold.

			RBT					
			YOY			Adult		
			Density	Biomass	K	Density	Biomass	K
BKT	YOY	Density τ	-0.12	-0.20	-0.18	-0.14	-0.18	0.01
		p-value	0.13	0.01	0.04	0.06	0.02	0.84
		N	86	85	59	88	88	86
		Biomass τ	-0.06	-0.11	-0.11	-0.09	-0.13	0.01
		p-value	0.46	0.16	0.22	0.20	0.09	0.88
		N	86	85	59	88	88	86
	K	τ	0.01	0.01	0.32	0.01	0.02	0.11
		p-value	0.87	0.87	0.00	0.86	0.85	0.18
		N	65	64	41	67	67	66
	Adult	Density τ	-0.37	-0.44	-0.29	-0.25	-0.30	-0.01
		p-value	0.00	0.00	0.00	0.00	0.00	0.90
		N	88	87	61	90	90	88
		Biomass τ	-0.40	-0.46	-0.26	-0.28	-0.31	0.02
		p-value	0.00	0.00	0.00	0.00	0.00	0.81
		N	88	87	61	90	90	88
	K	τ	-0.23	-0.24	0.09	-0.21	-0.19	0.21
		p-value	0.00	0.00	0.34	0.00	0.01	0.00
		N	83	82	56	85	85	83

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