

Smoky Mountains Water Quality Annual Report for 2001

R. Bruce Robinson, Ph.D., P.E.
Professor of Civil and Environmental Engineering

John Shubzda
Research Assistant

Thomas Barnett
Graduate Research Assistant

**Department of Civil and Environmental Engineering
The University of Tennessee
Knoxville, TN 37996
(865) 974-7730**

April 22, 2002

**Report Prepared For:
The National Park Service
Cooperative Agreement No.: 1443-CA-5460-98-006**

Smoky Mountains Water Quality Annual Report for 2001

R. Bruce Robinson, Ph.D., P.E.
Professor of Civil and Environmental Engineering

John Shubzda
Research Assistant

Thomas Barnett
Graduate Research Assistant

**Department of Civil and Environmental Engineering
The University of Tennessee
Knoxville, TN 37996
(865) 974-7730**

April 22, 2002

**Report Prepared For:
The National Park Service
Cooperative Agreement No.: 1443-CA-5460-98-006**

TABLE OF CONTENTS

	Page
1. Noland Divide Annual Deposition Rates	1
2. Stream Survey Results	4
2.1 pH	4
2.2 Acid Neutralizing Capacity	6
2.3 Conductivity	10
2.4 Nitrate	10
2.5 Sulfate	14
2.6 Chloride	14
2.7 Sodium and Potassium	16
2.8 Ammonium	16
2.9 Magnesium and Calcium	16
3. Overall QA/QC Procedures	23
3.1 Ion Chromatography QA/QC Procedures	24
3.2 Atomic Absorption QA/QC Procedures	28
3.3 Ion Balance	31
3.4 Inter-laboratory Comparison Results	31
3.5 Data Completeness	33
Appendix A-1: Water Quality Analysis of Calcium and Magnesium in the Great Smoky Mountains National Park, 2001	
Appendix A-2: Abstract of Report Entitled: Water Quality Characteristics, Temporal Trends, and Influencing Factors for Selected Streams in the Great Smoky Mountains National Park	

List of Tables

Table 2-1. Table 2-1. Possible ecological consequences of low surface water pH	5
Table 2-2. Summary of acidic level of water at sampled sites	9
Table 3-1. Analytical procedures for chemistry analysis performed at the University of Tennessee	23
Table 3-2. QA\QC results of the IC analysis for selected anions	24
Table 3-3. QA\QC results of the IC analysis for monovalent cations	25
Table 3-4. Average QA\QC results of the AA analysis for magnesium and calcium	28
Table 3-5. Average ion balances for both streamlets, precipitation and throughfall	31
Table 3-6. Individual scores of each analyte submitted to the USGS analytical evaluation program. All concentration data given in ppm, and conductivity given in $\mu\text{S}/\text{cm}$.	32
Table 3-7. Wet-only and throughfall measurements and estimates for annual precipitation amounts entering the NDW in 2001	33

List of Figures

Figure 1-1. Total Inorganic nitrogen deposition entering the NDW as throughfall and wet-only precipitation	2
Figure 1-2. Total sulfate entering the NDW as throughfall and wet-only precipitation	3
Figure 1-3. Total annual throughfall and wet-only precipitation volumes entering the NDW	3
Figure 2-1. Variability of pH in sampled GRSM streams	7
Figure 2-2. Regression analysis of median pH in sampled GRSM streams	7
Figure 2-3. Regression analysis of median pH in sampled GRSM streams without Cades Cove sites	8
Figure 2-4. Variability of acid neutralizing capacity in sampled GRSM streams	11
Figure 2-5. Scatter plot of median acid neutralizing capacity in sampled GRSM streams	11

Figure 2-6. Scatter plot of median acid neutralizing capacity in sampled GRSM streams without Cades Cove sites	12
Figure 2-7. Scatter plot of median conductivity in sampled GRSM streams	12
Figure 2-8. Variability of nitrate in sampled GRSM streams	13
Figure 2-9. Scatter plot of median nitrate in sampled GRSM streams	13
Figure 2-10. Variability of sulfate in sampled GRSM streams	15
Figure 2-11. Scatter plot of median sulfate in sampled GRSM streams	15
Figure 2-12. Scatter plot of median chloride in sampled GRSM streams	18
Figure 2-13. Scatter plot of median sodium in sampled GRSM streams	18
Figure 2-14. Scatter plot of median potassium in sampled GRSM streams	19
Figure 2-15. Variability of ammonium in sampled GRSM streams	19
Figure 2-16. Variability of magnesium in sampled GRSM streams	20
Figure 2-17. Scatter plot of median magnesium in sampled GRSM streams	20
Figure 2-18. Variability of calcium in sampled GRSM streams	21
Figure 2-19. Scatter plot of median calcium in sampled GRSM streams	21
Figure 2-20. Scatter plot of median magnesium in sampled GRSM streams without Cades Cove sites	22
Figure 2-21. Scatter plot of median calcium in sampled GRSM streams without Cades Cove sites	22
Figure 3-1. Nitrate concentrations made on laboratory check sample over multiple runs	26
Figure 3-2. Potassium concentrations made on laboratory check sample over multiple runs	27
Figure 3-3. Magnesium standard check sample results plotted over the course of the analysis	29
Figure 3-4. Calcium standard check sample results plotted over the course of the analysis	30

This report describes calendar year (CY) 2001 work accomplished under Amendment No. 6 to Cooperative Agreement No. 1443-CA-5460-98-006 between the National Park Service and the University of Tennessee for 'Water Quality Monitoring in the Great Smoky Mountains National Park'.

1. Noland Divide Annual Deposition Rates

During the year 2001, the amount of total inorganic nitrogen entering the Noland Divide Watershed (NDW) as throughfall was 692 equivalents of nitrogen per hectare per year (eq/ha/yr), and 335 (eq/ha/yr) was collected as wet-only precipitation (see Figure 1-1). These deposition rates were much lower than the overall deposition rates recorded since the project began in 1991. As data becomes available from other monitoring sites in the region, these data will be compared for consistency.

This same apparent annual trend was not evident in the sulfate deposition rates entering the NDW in 2001, 1830 (eq/ha/yr). In fact, the deposition of sulfate actually increased from last year, but remained close to the overall average (Figure 1-2). The difference between precipitation inputs and throughfall inputs represents a very good estimate of the dry and cloudwater inputs to these systems (Shubzda *et al.*, 1995). Unlike nitrogen, sulfate flux represents a very good estimate of the total deposition rate entering a watershed, because foliar uptake and/or leaching is minimal (Garten *et al.*, 1988; Lindberg and Garten, 1988).

The annual rainfall amount collected during 2001 was 199 cm, while surrounding lowland areas such as Knoxville, TN generally average around 109 cm/yr (Figure 1-3). This difference in precipitation volume can be attributed to orographic effects. Orographic precipitation occurs as

moist air is forced over mountains, the vapor pressure decreases, and the moist air reaches a saturation point, where increased precipitation occurs (Barry and Schemenauer, 1986).

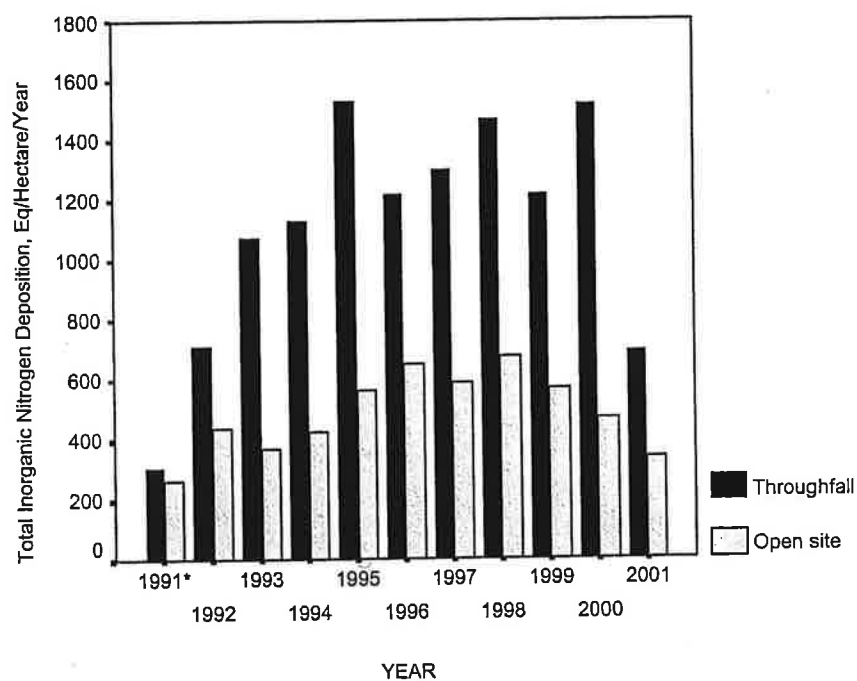


Figure 1-1. Total Inorganic nitrogen deposition entering the NDW as throughfall and wet-only precipitation. *The collections in 1991 started in June, and represent only half of the years total deposition rates.

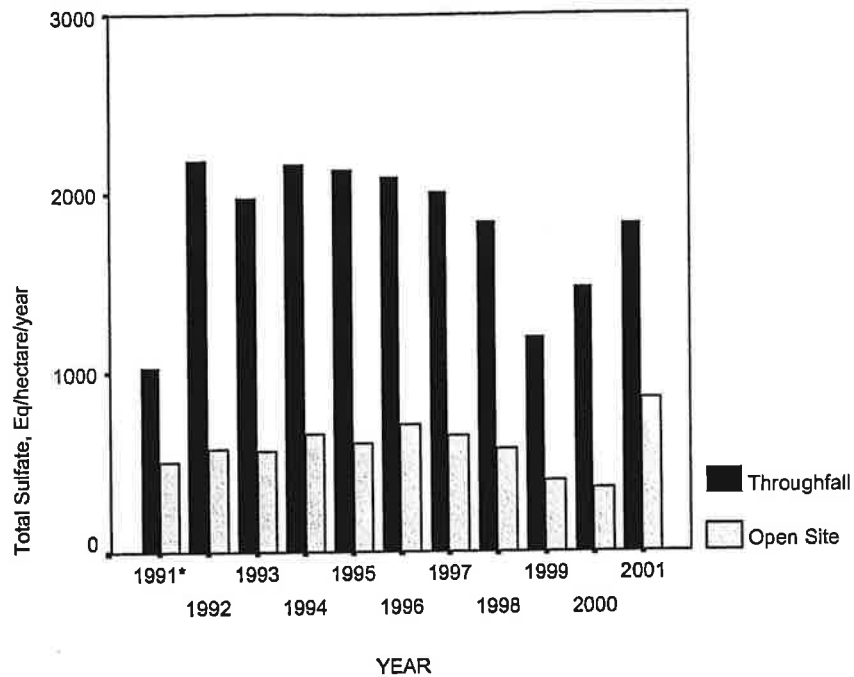


Figure 1-2. Total sulfate entering the NDW as throughfall and wet-only precipitation. *The collections in 1991 started in June, and represent only half of the years total deposition rates.

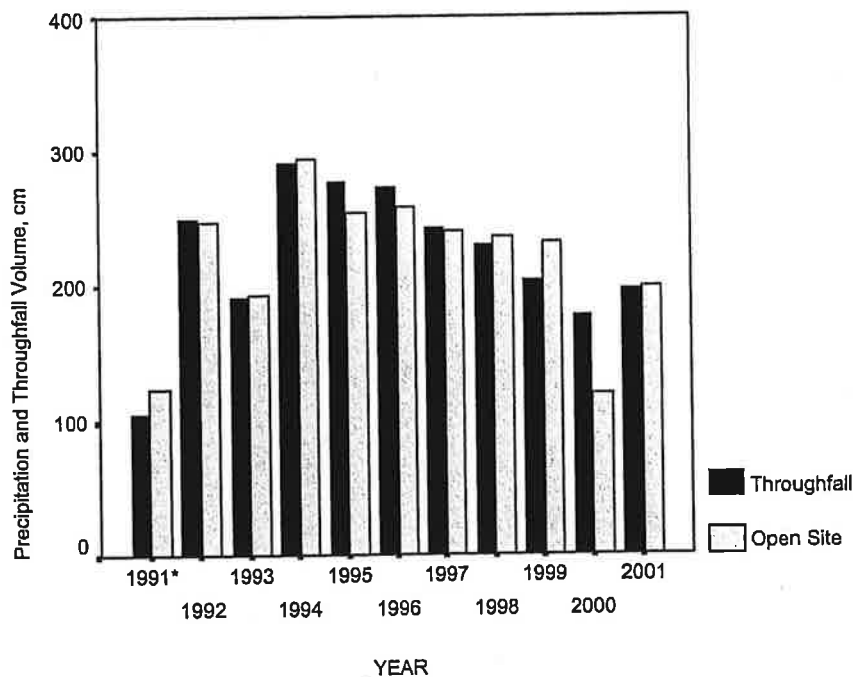


Figure 1-3. Total annual throughfall and wet-only precipitation volumes entering the NDW. *The collections in 1991 started in June, and represent only half of the total deposition rates.

2. Stream Survey Results

The following analyses utilize the chemistry data of collected samples from ninety sites within the GRSM. The data set includes samples collected from October, 1993 to November, 2001. Throughout the following text, comparisons will be made to previous work performed by Glenn Harwell, whose data set included samples collected from October, 1993 to October, 1998. Few valid calcium and magnesium data were available in earlier reports, so this report is the first to be able to show data and trends for these cations which are included at the end of this section.

2.1 pH

Stream water pH is one of the most important water quality parameters measured in the GRSM. It is a good indicator of the stream health, which includes the stream's ability to sustain aquatic life. Table 2-1 lists several pH ranges, potential biological effects, and the percentage of sample sites with median pH within those ranges although the reader should understand that many of the low pH streams are too small to support trout, that four sites are springs, and that many other factors are also important for aquatic organisms. Based on the 1993-2001 data for all sites including springs, eighty percent of the sampling sites have a median pH less than a value of 6.5, below which can adversely affect sensitive aquatic organisms. This is up from the 77% of sampling sites with pH less than 6.5 found in previous work by Harwell. Other pH comparisons can be made between current data and Harwell's results in table 2-1.

The median pH of sampled sites within the Park appears to increase with decreases in elevation. The box plots in figure 2-1 show this trend in pH by different sample site elevation ranges. Simple linear regression performed on the data indicates a statistically significant ($p < 0.10$) trend in pH with elevation. The scatter plot, trend line, and regression equation are

Table 2-1. Possible ecological consequences of low surface water pH.

Source: Baker, J.P., J. Van Sickle, C.J. Gagen, D.R. DeWalle, W.E. Sharpe, R.F. Carline, B.P. Baldigo, P.S. Murdoch, D.W. Bath, W.A. Krester, H.A. Simonin, and P.J. Wigington, Jr., Episodic acidification of small streams in the northeastern United States: effects on fish populations, *Ecological Applications*, 6, 422-437.

pH range	Biological effects	Percentage of sample sites with median pH within range (1993-98 data)	Percentage of sample sites with median pH within range (1993-2001 data)
> 6.5	No adverse effects	23	20.0
6.0 - 6.5	Loss of sensitive benthic invertebrates	56	60.0
5.5 - 6.0	Loss of acid-sensitive fish Reduced reproduction in sensitive fish species Increase in green algae in periphyton	13	13.3
5.0 - 5.5	Loss of most fish species Green algae dominate periphyton Loss of most mayflies, stoneflies, caddisflies, and shellfish Reduced biomass and productivity	5	4.4
< 5.0	Loss of all fish species Decreased nutrient cycling rates Decline in periphyton species richness Decline in benthic invertebrates Reproductive failure of acid-sensitive amphibians	3	2.2

displayed in figure 2-2. Elevation explains 51 percent of the variability in pH ($r^2=0.51$) which is identical to the results found from the 93-98 data set. However, the regression equation obtained from the current data set is quite different from the previous work. The regression equation obtained from the 93-98 data is as follows:

$$\text{Median pH} = -9.452 \text{ E-04 (elevation)} + 7.078.$$

And the equation using current data is:

$$\text{Median pH} = -9.237 \text{ E-04 (elevation)} + 7.053,$$

where elevation is in meters above sea level. As can be seen, the elevation trend has changed very little with the additional three years of data. The slopes and intercepts offer only a 2.3 % and 3.5 % difference, respectively. When three sampling sites from Cades Cove, which have significantly higher pH, are removed from the data set (sites 156, 174, 489), the resulting regression equation (see figure 2-3) is:

$$\text{Median pH} = -8.338 \text{ E-04 (elevation)} + 6.946,$$

which again compares closely with the 93-98.

2.2 Acid Neutralizing Capacity

The variability of acid neutralizing capacity within the GRSM is similar to that of pH because pH values are positively correlated with ANC. Table 2-2 lists the ANC ranges that are commonly cited to classify the acidic level of a surface water, its classification, and the percentage of sample sites within each range for the 93-98 data and the current data. It can be seen that 87 of the 90 sites (about 97%) including springs are classified as either sensitive, extremely sensitive, or acidic. The most notable difference between the 93-98 and the current results are that three of the sites (site numbers 143, 215, and 336) that were classified sensitive are now classified as extremely sensitive and only site number 4, that was classified as

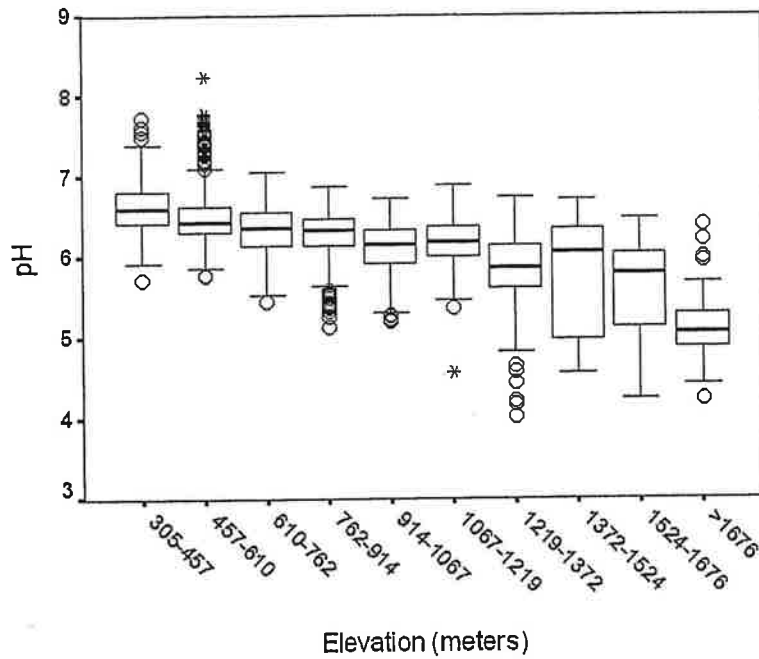


Figure 2-1. Variability of pH in sampled GRSM streams

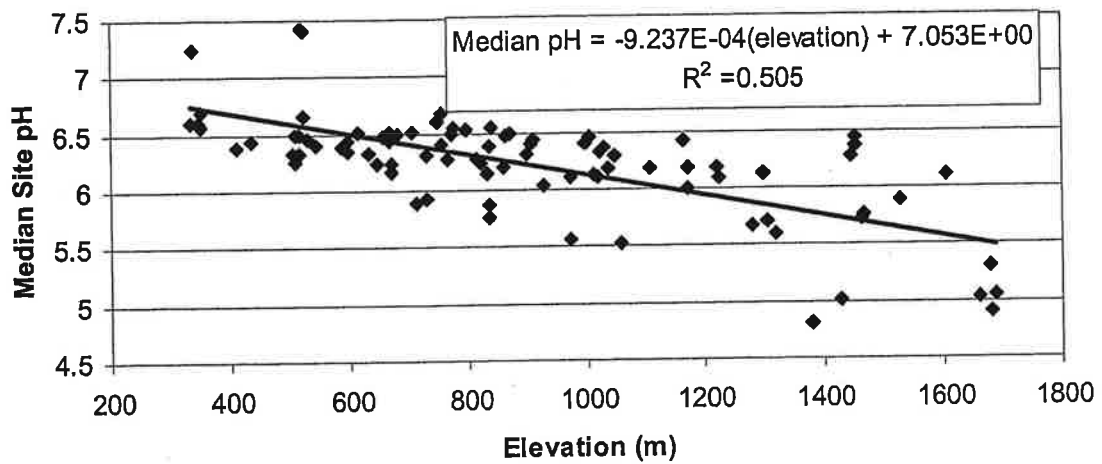


Figure 2-2. Regression analysis of median pH in sampled GRSM streams.

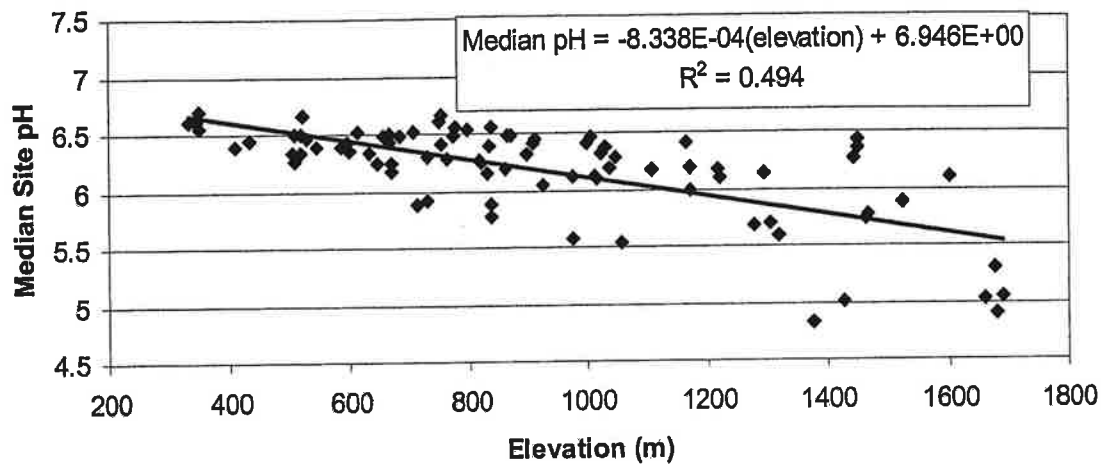


Figure 2-3. Regression analysis of median pH in sampled GRSM streams without Cades Cove sites.

Table 2-2. Summary of acidic level of water at sampled sites.

Source: Webb, J.R., B.J. Cosby, J.N. Galloway, and G.M. Hornberger, Acidification of Native Brook Trout Streams in Virginia, *Water Resources Research*, 25(6), 1,367-1,377.

ANC range ($\mu\text{eq/L}$)	Classification	Percentage of sample sites with median ANC within range (1993-98 data)	Percentage of sample sites with median ANC within range (1993-2001 data)
< 0	acidic	4 to 5	4.4
0 - 50	extremely sensitive	52	54.4
50 - 200	sensitive	40	37.7
> 200	not classified	3	3.3

extremely sensitive is now classified as sensitive. Although these sites changed classification, they remain on the borderline between classifications.

Figure 2-4 shows the box plot of median ANC versus elevation class and figure 2-5 shows the scatter plot of median ANC versus elevation. Like pH, ANC increases with decreasing elevation. Both the intercept and the slope prove to be statistically significant when simple linear regression is performed on the data in figure 2-5, but the equation does not explain much of the variability in ANC ($r^2=0.11$). However, when the Cades Cove sites are excluded (see figure 2-6), the equation explains 38 percent of the variability in median pH. These results are similar to those with 93-98 data set.

2.3 Conductivity

Eighty-five of the ninety sampling sites (about 95%) within the GRSM have conductivity values less than 25 micro siemens, which indicates that the majority of waters in the park have low ionic strengths. Figure 2-7 is a scatter plot of median conductivity versus elevation. There was no statistically significant relationship found between the two.

2.4 Nitrate

Figures 2-8 and 2-9 show a significant trend in nitrate concentrations with elevation. The median nitrate concentrations increase with increases in elevation. Regression analysis of median nitrate versus elevation reveals a statistically significant trend with an r-square equal to 0.48. However, the regression equation yields an intercept of -8.101, which gives negative nitrate concentrations for elevations below 253 meters. Therefore, this equation could not be used to predict nitrate concentrations at elevations below 253 meters. Results from the 93-98

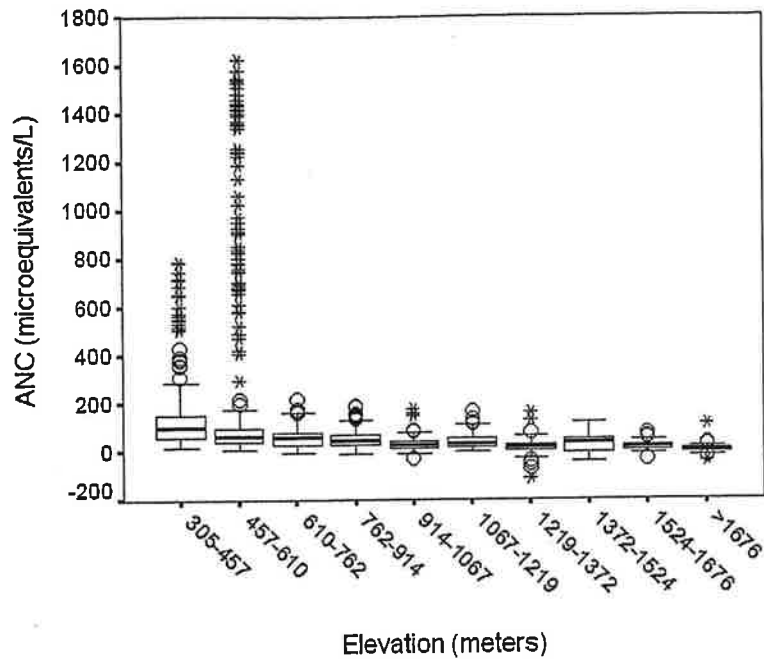


Figure 2-4. Variability of acid neutralizing capacity in sampled GRSM streams.

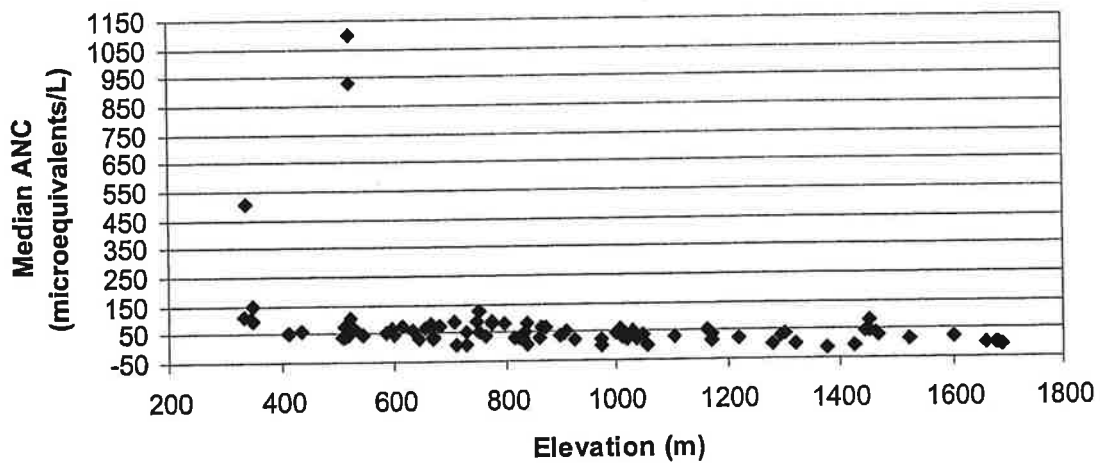


Figure 2-5. Scatter plot of median acid neutralizing capacity in sampled GRSM streams.

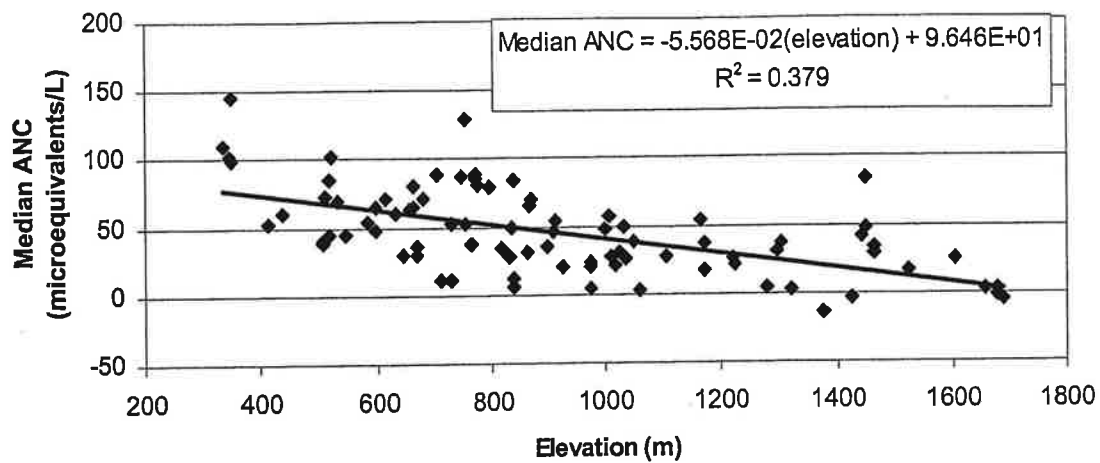


Figure 2-6. Scatter plot of median acid neutralizing capacity in sampled GRSM streams without Cades Cove sites.

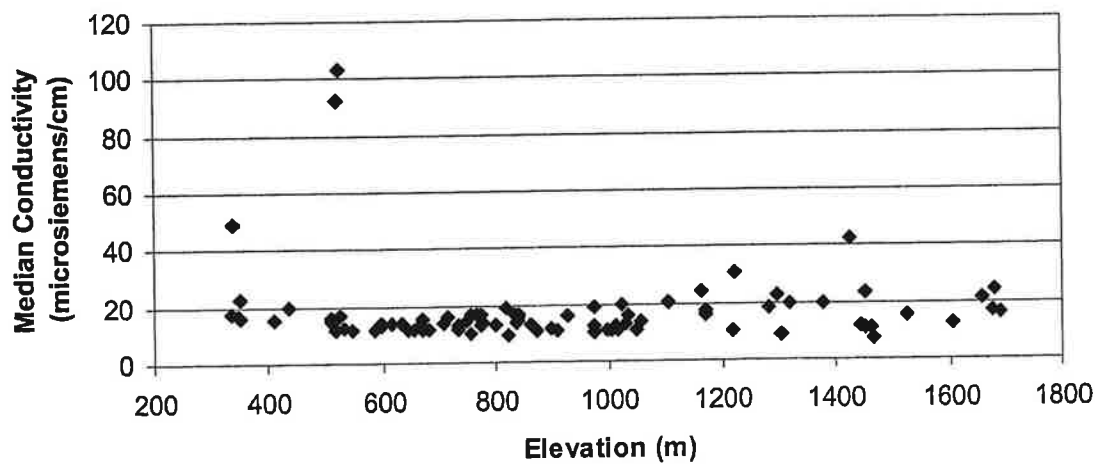


Figure 2-7. Scatter plot of median conductivity in sampled GRSM streams.

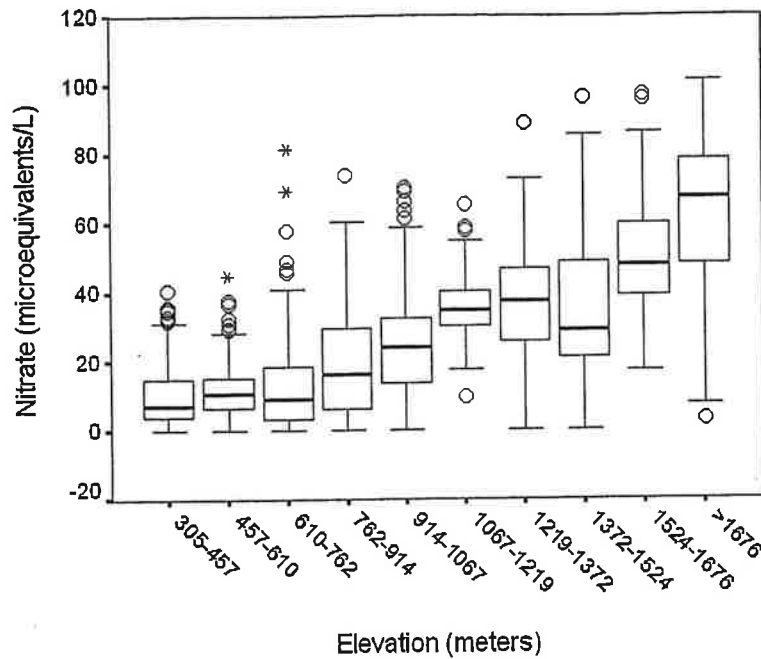


Figure 2-8. Variability of nitrate in sampled GRSM streams.

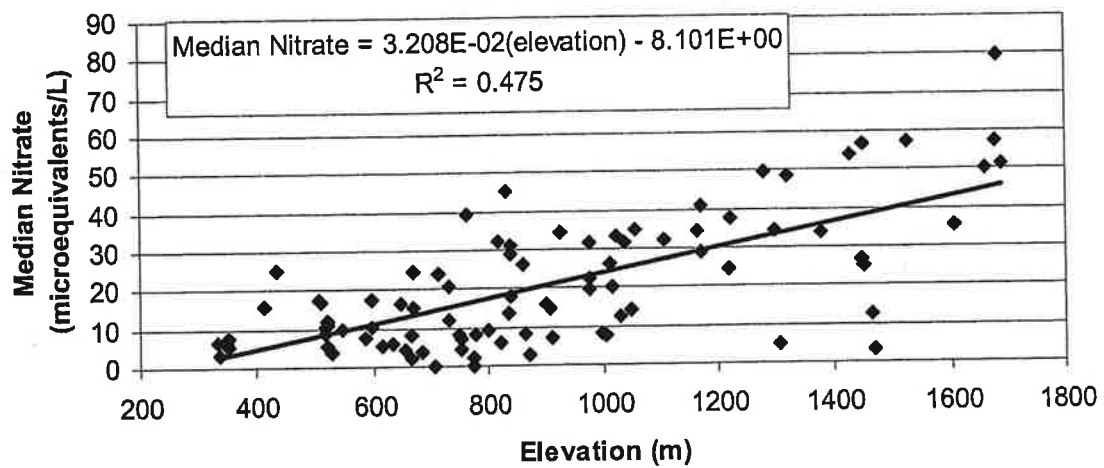


Figure 2-9. Scatter plot of median nitrate in sampled GRSM streams.

data yielded an intercept that gave negative nitrate concentrations for elevations below 255 meters.

Elevational nitrate trends for the 93-01 data are very similar to the 93-98 data. The regression equation obtained from the 93-98 data is:

$$\text{Median nitrate} = 3.301 \text{ E-02 (elevation)} - 8.423$$

whereas the equation using 93-01 data is:

$$\text{Median nitrate} = 3.207 \text{ E-02 (elevation)} - 8.098$$

2.5 Sulfate

Median sulfate concentrations appear to increase with elevation up to about 1372 meters, but then begin to decrease and remain fairly constant with increases in elevation. This is illustrated in figure 2-10. Regression analysis (see figure 2-11 for scatter plot) proved both the slope and intercept, from the resulting equation, to be statistically significant ($p < 0.10$). However, only 3.9 % of the variability in sulfate is explained by elevation indicating that elevation alone is not a good predictor of sulfate concentrations. The slope term of the resulting regression equation is positive, which indicates that sulfate concentrations might increase with elevation. These results agree closely with those obtained with the 93-98 data. Of course somewhat higher sulfate concentrations are found in elevations with significant Anakeesta as discussed by Harwell.

2.6 Chloride

The majority of sampling sites within the GRSM (about 97 %) have median chloride concentrations less than 20 micro equivalents per liter and show very little variability with elevation. A scatter plot of median chloride concentration versus elevation can be seen in figure 2-12. Regression analysis of this data did not yield a statistically significant trend. These

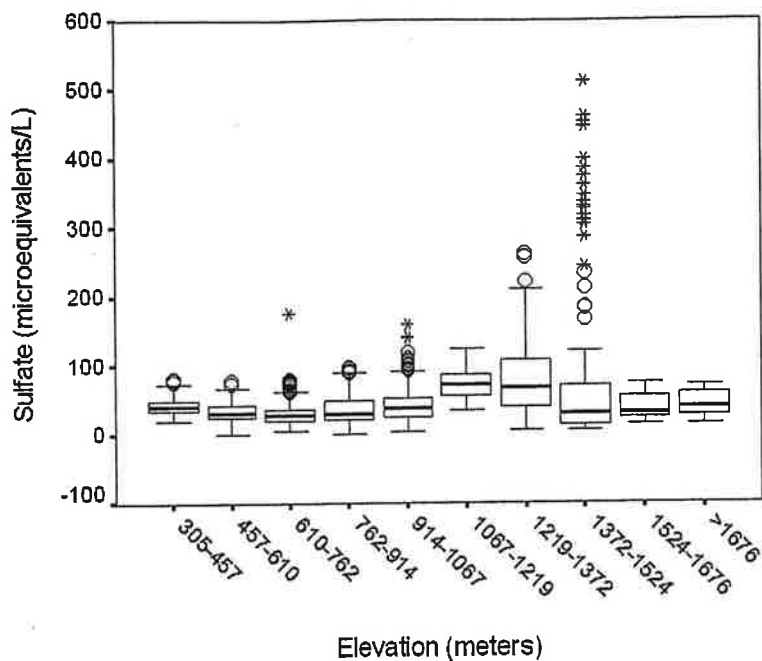


Figure 2-10. Variability of sulfate in sampled GRSM streams.

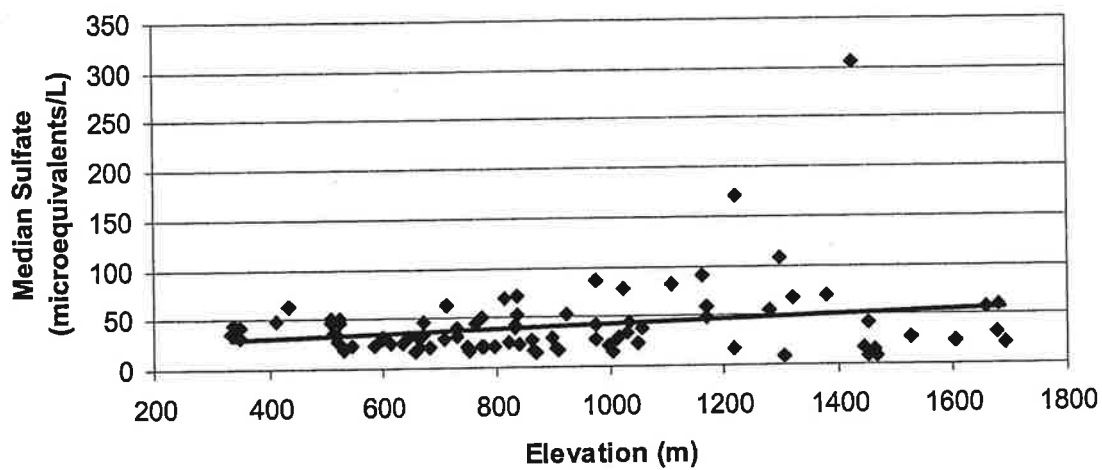


Figure 2-11. Scatter plot of median sulfate in sampled GRSM streams.

results are similar to those of previous work.

2.7 Sodium and Potassium

Figures 2-13 and 2-14 show scatter plots of median sodium and potassium concentrations versus elevation. Regression analysis reveals statistically significant trends for both sodium and potassium, but only 18 and 8 percent, respectively, of the of the variability in concentrations are explained by elevation. Regression equations for both constituents yield negative slopes, indicating that their concentrations decrease with increases in elevation. These results are nearly identical to those obtained with the 93-98 data set.

2.8 Ammonium

The median ammonium ion concentrations for every sampling site are below our detection limit. However, figure 2-15, which presents box plots of ammonium concentration versus elevation class, does show that ammonium concentrations above the detection limit are occasionally encountered.

2.9 Magnesium and Calcium

Median concentrations of magnesium and calcium are similar in that neither show significant trends with elevation. Figures 2-16 through 2-19 present this graphically. From figures 2-16 and 2-18, it can be seen that median concentrations of magnesium and calcium remain fairly constant with elevation with the exception of three sampling sites on Abrams creek within Cades Cove. These sites have relatively high concentrations of magnesium and calcium most likely because of underlying limestone geology. Figures 2-20 and 2-21 present scatter plots of the data with the exclusion of the Cades Cove sites. Statistical analysis of this data yields an average of the median

calcium concentrations of 54.8 $\mu\text{eq/L}$ with a standard deviation of 20.7 $\mu\text{eq/L}$ and an average of 27.5 $\mu\text{eq/L}$ with a standard deviation of 12.2 $\mu\text{eq/L}$ for magnesium.

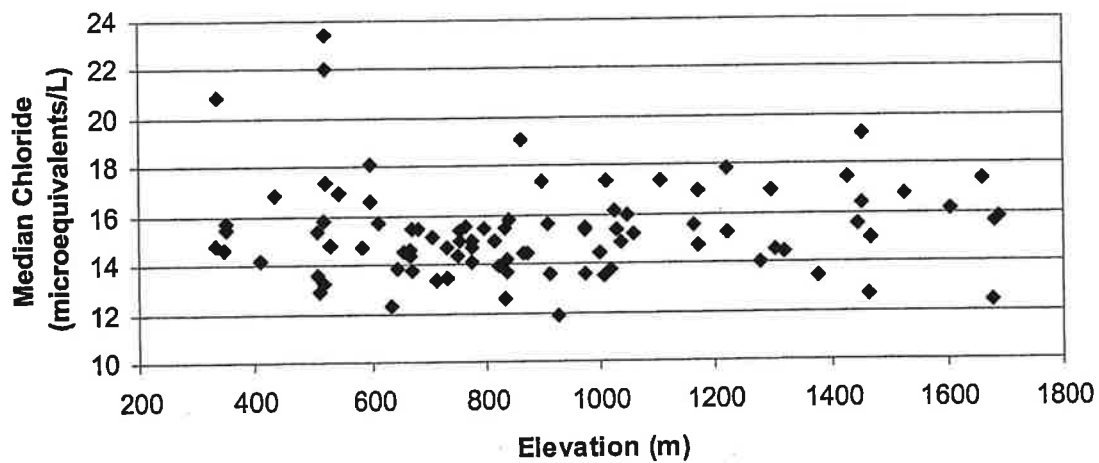


Figure 2-12. Scatter plot of median chloride in sampled GRSM streams.

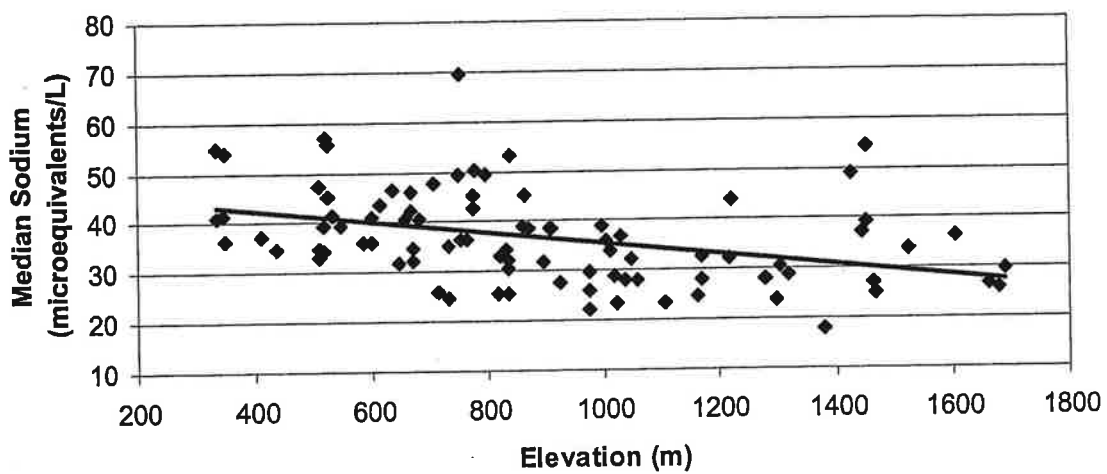


Figure 2-13. Scatter plot of median sodium in sampled GRSM streams.

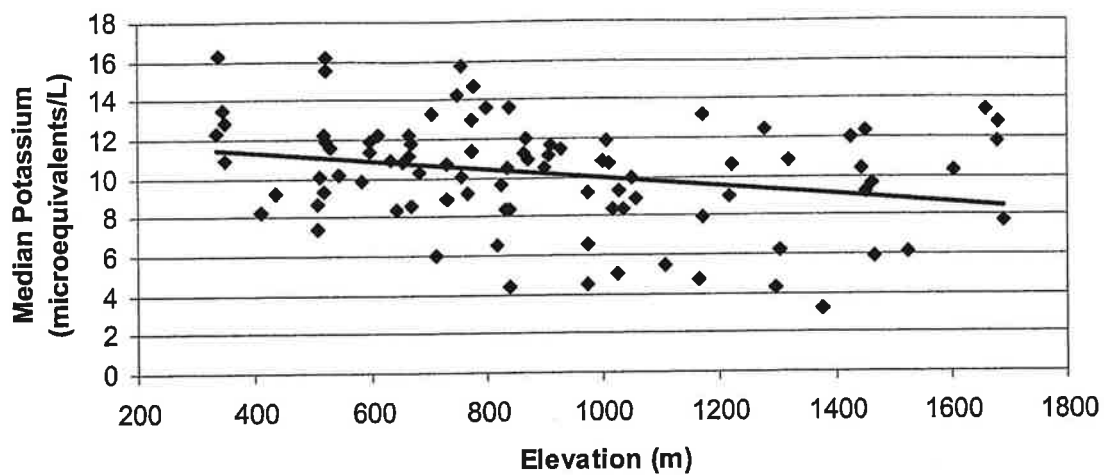


Figure 2-14. Scatter plot of median potassium in sampled GRSM streams.

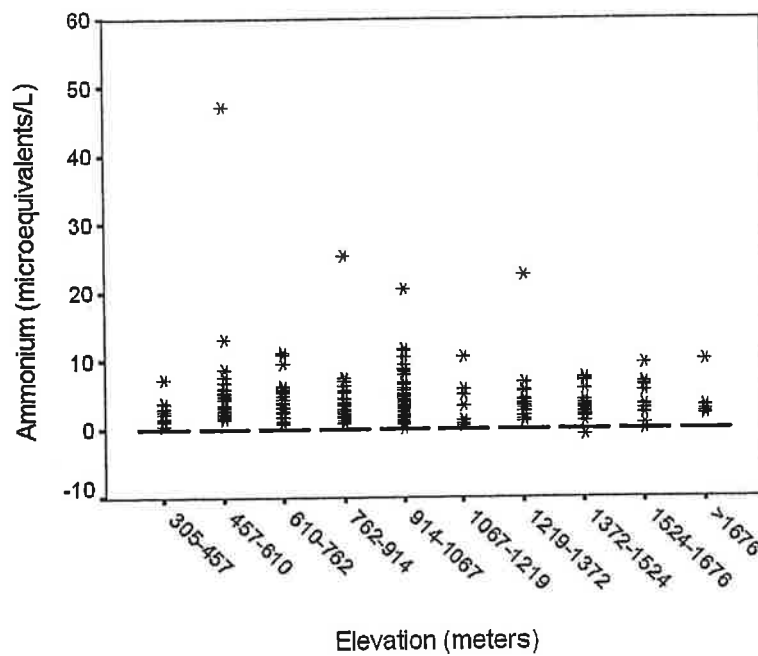


Figure 2-15. Variability of ammonium in sampled GRSM streams.

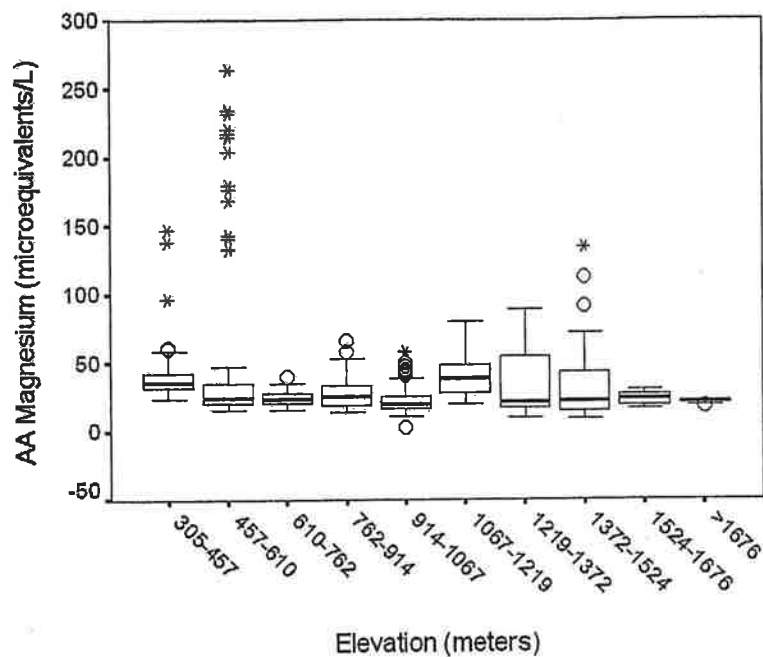


Figure 2-16. Variability of magnesium in sampled GRSM streams.

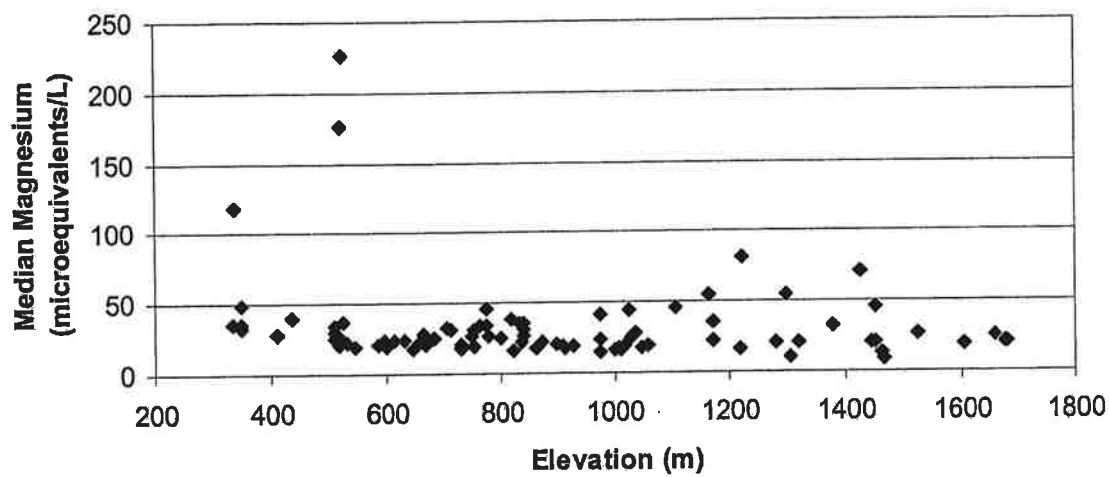


Figure 2-17. Scatter plot of median magnesium in sampled GRSM streams.

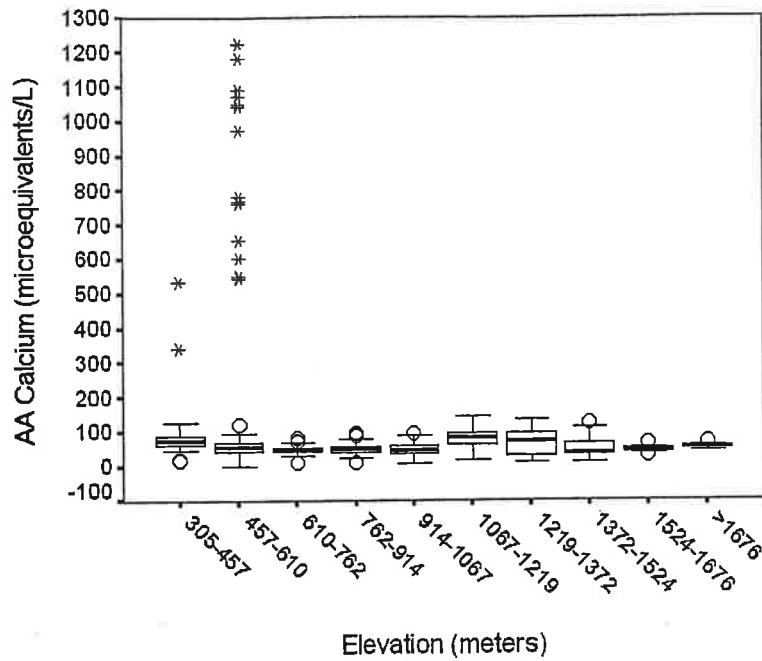


Figure 2-18. Variability of calcium in sampled GRSM streams.

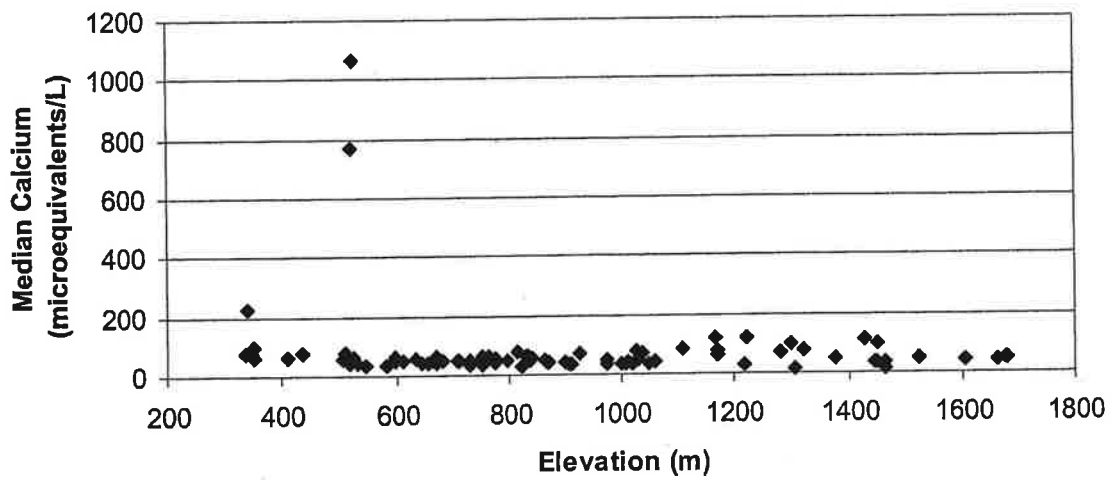


Figure 2-19. Scatter plot of median calcium in sampled GRSM streams.

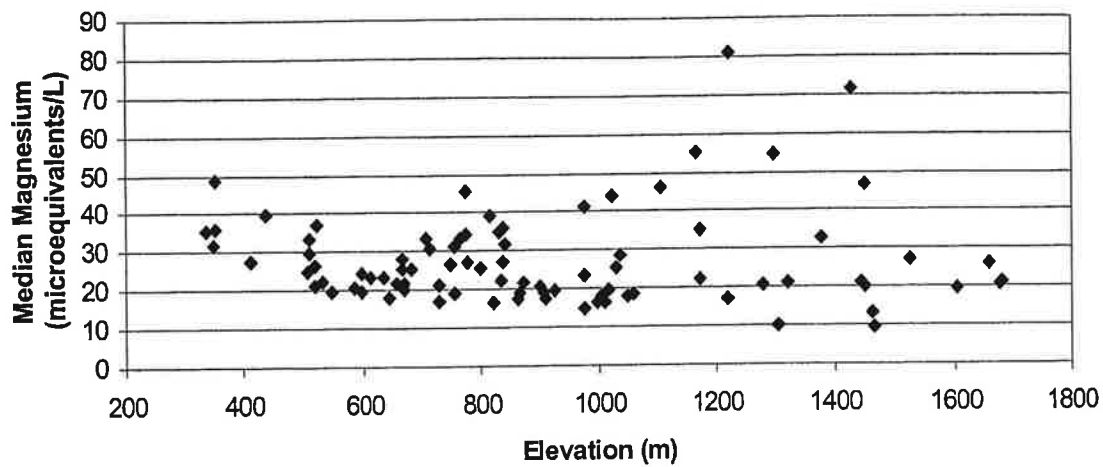


Figure 2-20. Scatter plot of median magnesium in sampled GRSM streams without Cades Cove sites.

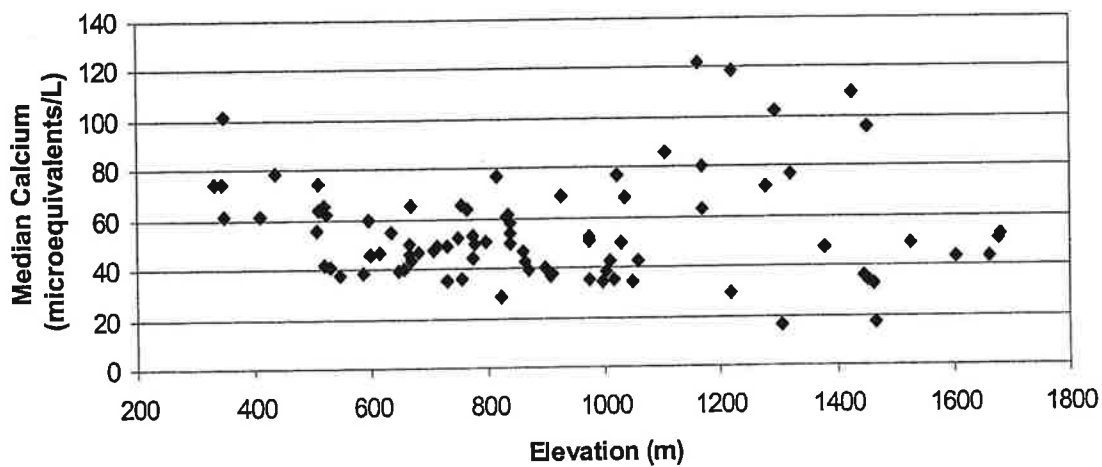


Figure 2-21. Scatter plot of median calcium in sampled GRSM streams without Cades Cove sites.

3. Overall QA\QC Procedures

All procedures used to chemically analyze water samples are based upon standard published methods (Table 3-1). These procedures are used for the analysis of stream water, precipitation, and throughfall. Since the instruments and procedures are optimized for samples of low concentrations of dissolved constituents, dilution is used when necessary on higher concentration samples (e.g. throughfall). The samples are analyzed at room temperature to standardize the results among samples from different locations that may have been collected at different times and temperatures. Once pH, conductance, and ANC (Acid Neutralizing Capacity) have been obtained, samples are refrigerated until the other analysis are performed.

Table 3-1. Analytical procedures for chemistry analysis performed at the University of Tennessee.

Analysis	Procedure	Equipment	Method References
pH	Potentiometric	Radiometer Auto-titrator	EPA Method 150.1
Conductance	Potentiometric	Jenway Model 4010 Conductance Meter	EPA Method 120.1
Acid Neutralizing Capacity (ANC)	Automated Titration	Radiometer Auto-titrator	Automated Gran Titration for low ionic strength waters, as in Hillman et al. 1986
Anions (NO_3^- , Cl^- , SO_4^{2-})	Ion Chromatography	Dionex Ion Chromatograph	Standard Methods 4110
Monovalent Cations (Na^+ , K^+ , NH_4^+)	Ion Chromatography	Dionex Ion Chromatograph	Manufacturers Protocols
Divalent Cations (Ca^{2+} , Mg^{2+})	Atomic Absorption	Instrumentation Laboratory	Standard Methods 3111 Manufacturers Protocols

3.1 Ion Chromatography QA\QC Procedures

Several QA\QC procedures are performed when running the IC. These procedures were developed to optimize the performance of the IC. The IC is fully automated. Once the samples are in the auto-sampler, the machine performs the analyses and the results are computed and placed in Excel spreadsheets. All deionized water used for standards and reagents are tested for conductivity before use. The deionized water must have a conductivity of less than 1.0 $\mu\text{S}/\text{cm}$. Some of the QA\QC samples include; reagent blanks, sample acidification blanks (for cations only since anion samples are not acidified), and replicates. Table 3-2 summarizes the results of the QA\QC procedures followed during the operation of the IC for anions. Table 3-3 summarizes the results of the procedures followed during the tests for monovalent cations using the IC. Both tables indicated very good QA\QC procedures were followed during the analyses for anions and monovalent cations. In addition, a laboratory check sample is run with every set of IC analyses. Plotting the results of the multiple measurements made over time, insures cross comparisons of the results (Figure 3-1 and 3-2). Figure 3-1 shows multiple nitrate measurements during several different runs. Figure 3-2 shows multiple potassium measurements during several different runs. Both figures show very good precision with repeated measurements for those analytes.

Table 3-2. QA\QC results of the IC analysis for selected anions during a typical run.

QA\QC Procedure	Cl^-	NO_3^-	SO_4^{2-}
R-squared of the calibration curve	0.994	0.996	0.995
Reagent blanks	not detected	not detected	not detected
Absolute average value in % difference in replicates	3.45% (n=10)	3.98 % (n=10)	1.42 % (n=10)

Table 3-3. QA\QC results of the IC analysis for monovalent cations during a typical run.

QA\QC Procedure	Na ⁺	NH ₄ ⁺	K ⁺
R-squared of the calibration curve	0.995	0.986	0.997
Acidification blanks	not detected	not detected	not detected
Reagent blanks	not detected	not detected	not detected
Absolute average value in % difference in replicates	6.46% (n=10)	4.47 % (n=10)	0.68 % (n=10)

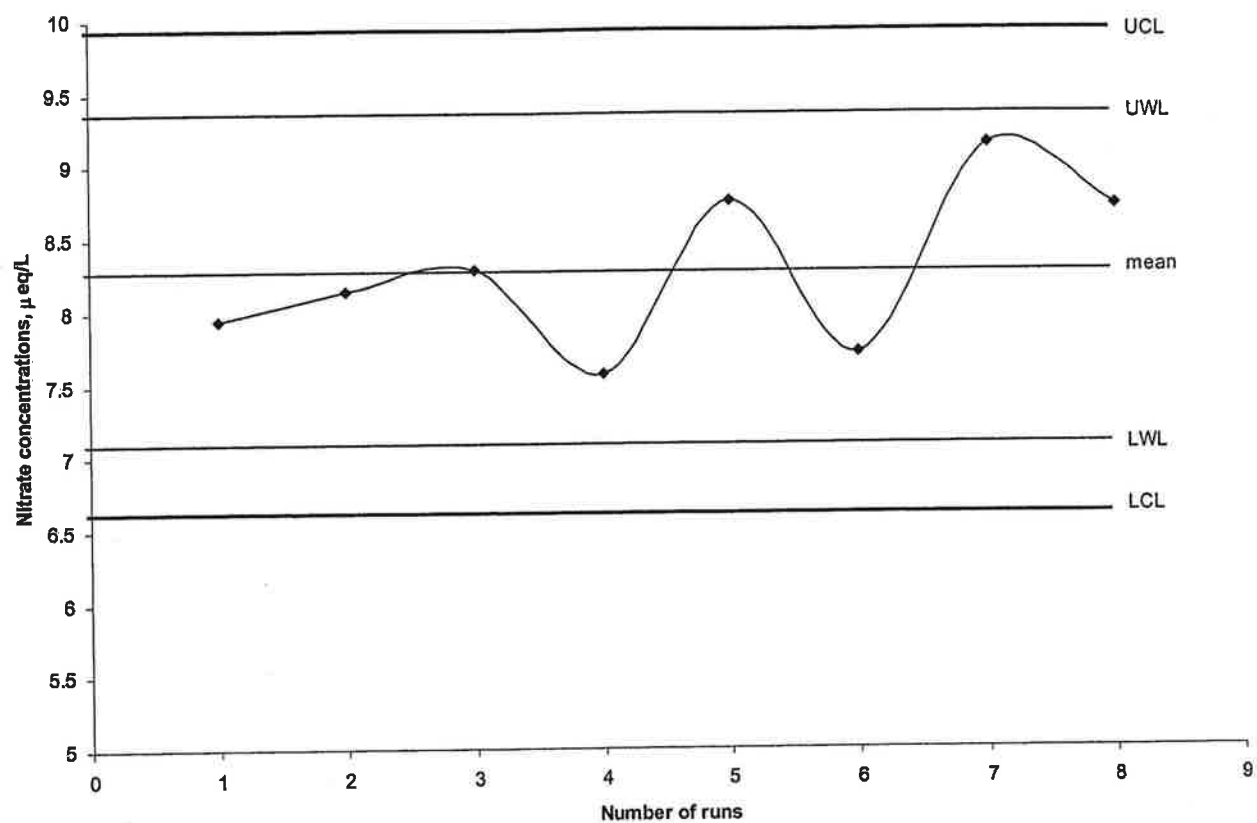


Figure 3-1. Nitrate concentrations made on laboratory check sample over multiple runs. UCL and LCL = upper and lower control limits (± 3 S.D.); UWL and LWL = upper and lower warning limits (± 2 S.D.).

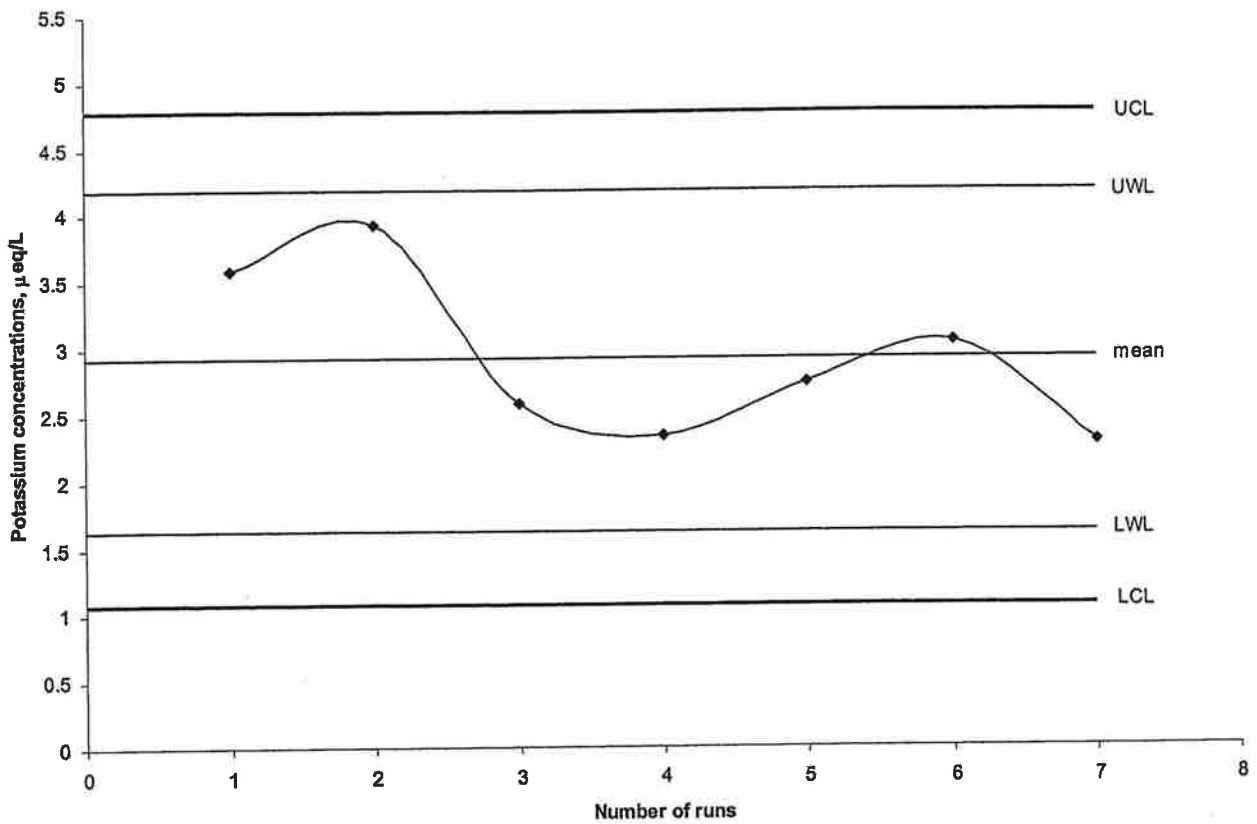


Figure 3-2. Potassium concentrations made on laboratory check sample over multiple runs. UCL and LCL = upper and lower control limits (± 3 S.D.); UWL and LWL = upper and lower warning limits (± 2 S.D.).

3.2 Atomic Absorption QA\QC Procedures

A series of QA\QC samples were employed during the analysis and closely monitored throughout the entire run of samples. These procedures are outlined in detail in a protocols document previously developed by the current investigators. Some of the QA\QC samples include; reagent blanks, sample acidification blanks, replicates, and spiked samples. The sample acidification blanks and reagent blanks showed no traces of Mg or Ca. Therefore, the samples were not contaminated by the acidification process or the ionization suppressant (Table 3-4). Replicates and spiked samples were also analyzed. A spike sample is a procedure where a known concentration is added to a sample and the difference between the un-spiked and spiked sample is measured. The difference divided by the expected is the % recovery. Table 3-4 shows very good QA\QC results with respect to % spike recoveries very close to 100%. A quality control “check” sample is also used during the analysis. This sample is a prepared standard which is run after every 10 to 20 samples. If this sample differs more than 5 % from the expected, the machine is re-calibrated. The results of the “check” sample show very little drift of the instrument (Figure 3-3 and 3-4).

Table 3-4. Average QA\QC results of the AA analysis for magnesium and calcium.

QA\QC Procedure	Mg	Ca
R-squared of the calibration curve	0.9999	0.9998
Acidification blanks	not detected	not detected
Reagent blanks	not detected	not detected
Absolute average value of % spike recoveries	98.46% (n=3)	104.56 % (n=3)

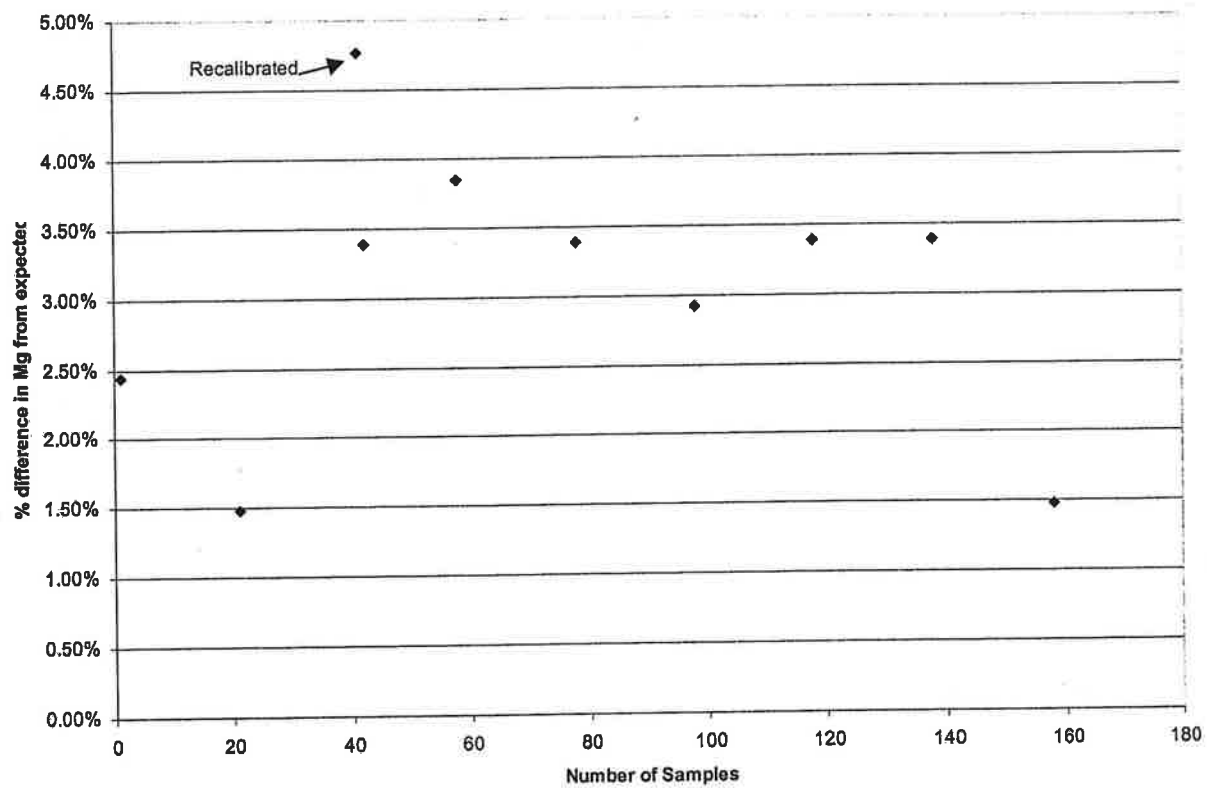


Figure 3-3. Magnesium standard check sample results plotted over the course of the analysis.

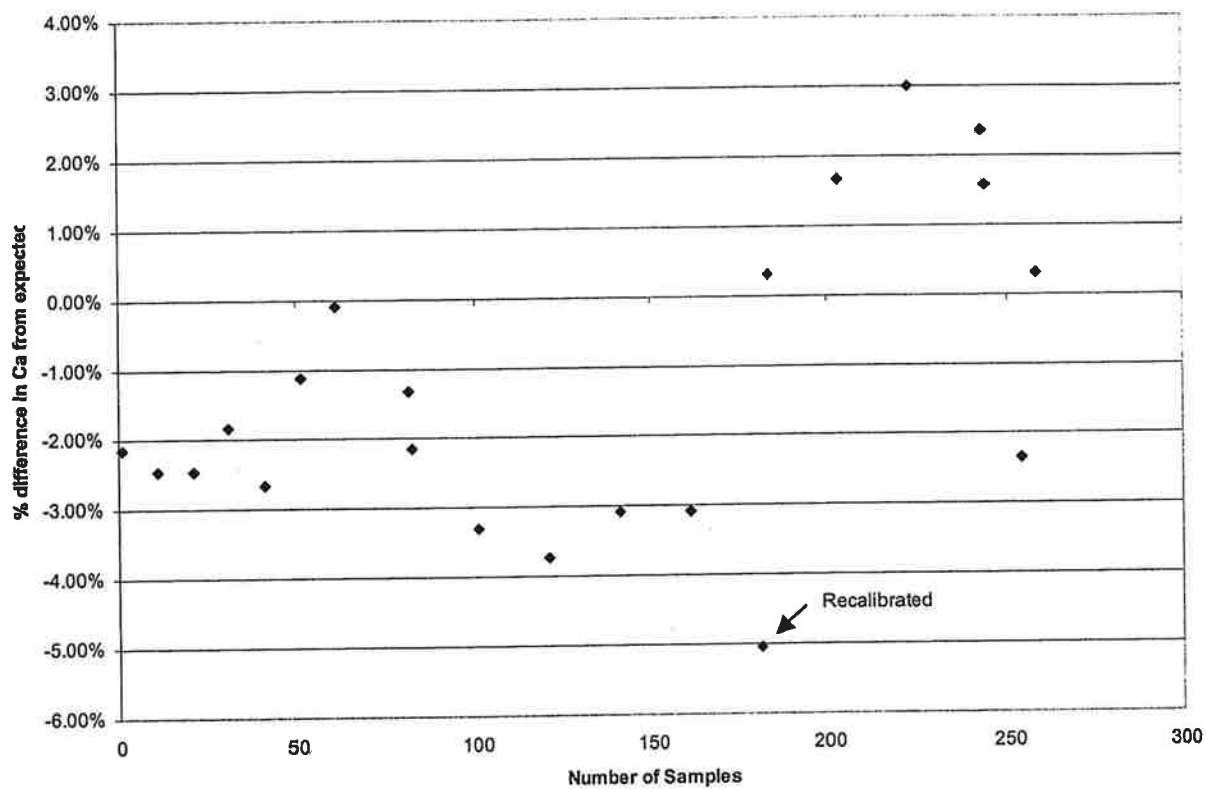


Figure 3-4. Calcium standard check sample results plotted over the course of the analysis.

3.3 Ion Balance

Once the all the analyses are performed, the results are entered into a spreadsheet and an ion balance or ion deficit for open site and throughfall is calculated as a final QA\QC procedure. An ion balance is calculated by summing up all the anions and cations in solution. This balance should be +/- 15 % according the US EPA recommend guidelines. Calculation of the ion balance or deficit is embedded in the Excel spreadsheets associated with each sampling site. Table 3-5 summarizes the results from both streamlets, along with the precipitation and throughfall measurements. The overall balance on all the sites is very close to zero, indicating good results have been obtained in the overall data.

Table 3-5. Average ion balances for both streamlets, and ion deficit for precipitation and throughfall.

	NE Streamlet	SW Streamlet	Open Site	Throughfall
% Ion balance	1.87%	3.42%	7.52%	1.35%

3.4 Inter-laboratory Comparison Results

Once a year, the project participates in the fall analytical evaluation program operated by the United States Geological Survey (USGS). This program provides a variety of standard reference samples to accomplish quality assurance testing at USGS and non-USGS laboratories. A series of samples are prepared and distributed each spring and fall, we generally only participate in the fall comparisons. The program began in 1962 from a single sample that was prepared and sent to twenty-three USGS laboratories. Currently, there are 270 USGS and non-USGS laboratories enrolled in the program.

Though this is not a laboratory certification program, participation in this quality assurance program is mandatory for all laboratories providing water-quality data for USGS sponsored reports

or storage in the USGS national databases. The results from these comparisons can be used to alert participating laboratories of possible deficiencies in their analytical operations. This program assigns an overall score from the results that a lab provides, and it also provides an individual rating for each analyte that is submitted and compared to the overall most probable number. The highest possible overall rating is 4.0 indicating excellent results, to a 0 for unsatisfactory results.

By participating in these type of round-robin comparison, the problems with using IC to analyzed magnesium and calcium became evident. Since we changed to AA analysis for our divalent measurements, our results have dramatically changed to very positive results. Our overall score for 2001, was 3.3, which was between and excellent and good on the USGS rating score.

Table 3-6. Individual scores or each analyte submitted to the USGS analytical evaluation program. All concentration data given in ppm, and conductivity given in $\mu\text{S}/\text{cm}$.

Analyte	pH	Conductance	Cl ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
MPV ¹	4.61	28.3	3.10	1.44	0.8	0.5	0.506	1.03
UT-results	4.58	28.28	3.04	1.23	0.82	0.452	0.471	1.01
Overall rating ²	4	4	4	2	4	2	2	4

1. Most probable values in the overall results.

2. Overall rating: 4 = excellent, 3 = good, 2 = satisfactory, 1.0 = marginal, and 0 = unsatisfactory.

The individual scores or each analyte are reported in Table 3-6. Overall, the program did not receive any score lower than 2.0, which is considered 'satisfactory' by USGS standards. This was the first time the program received acceptable results on all the analytes submitted.

3.5 Data Completeness

There are several types of data including stream survey and NDW grab samples; NDW

continuous monitors for pH, conductivity, and flow; the open site and throughfall collectors; and lysimeters.

Estimating the amount of completeness for the deposition monitoring stations must consider that samples are combinations of multiple rain events collected since the last visit to the site. Since these samples are unprotected they are vulnerable to animal interaction. In 2001, we lost one collection from the throughfall site because of bear damage. In addition, the wet-only collector (i.e. the Aerochem) uses a deep-cycle marine battery and rechargeable solar panels. During the winter months this becomes a difficult collection technique due to extreme temperatures. During 2001, we experienced three separate Aerochem malfunctions due to loss of power from extreme temperature. An estimated or calculated value are given for these missing collections and added to the annual totals amounts. From this adjusted total, a percentage of the actual total volumes collected can be calculated (Table 3-6).

Table 3-7. Wet-only and throughfall measurements and estimates for annual precipitation amounts entering the NDW in 2001.

	Wet-only precipitation	Throughfall
Missing volume ¹ , cm	5.61	4.39
Annual amount collected, cm	199.24	197.55
Estimated total annual amount, cm	204.85	201.94
Percentage of the estimated total that was collected	97.26 %	97.83 %

¹Missing volume estimates assume equal precipitation amounts between the adjacent throughfall and precipitation stations. If both stations were affected, then precipitation volume was taken from the weather station data set.

The continuous monitoring of stream pH and conductivity was interrupted on occasion due to either clogging of flow through sampling vessel port, loss of battery power, snow that dislodged electrical

connections, and malfunctioning units. We estimate that 90% of the continuous stream pH and conductivity was captured. We plan to begin keeping a running total of data completeness because going back through the data at the end of the year to calculate an exact completeness requires considerable time. Stream flow measurements are interrupted on occasion due to freezing of the flumes' stilling wells. We estimate that better than 95% of the 15-minute stream flow data were captured.

NDW lysimeter samples are collected except when the sample collection system freezes or animal interaction occurs.

Stream survey and NDW samples are collected except in the rare occasion when the sites are inaccessible (e.g., Round-bottom road occasionally has many fallen trees across the road) or the streams are dry. We estimate that over 95% of all analyses were obtained. It is very rare that a sample analysis fails due to spilled samples or other reasons.

It should also be noted that an extensive effort was made in November 2001 to QA/QC the data entries for the stream survey and NDW database. Statistical methods were used to identify potential outliers in the data. Those identified were checked and corrected if warranted by looking at the original data calibration curves, consistency with other analysis, etc.

Appendix A-1

Water Quality Analysis of Calcium and Magnesium in the Great Smoky Mountains National Park, 2001. A major effort to evaluate QA/QC issues for calcium and magnesium analysis was completed in 2001. Below is a summary of the findings

Executive summary

Water quality is monitored in the Great Smoky Mountains National Park by taking quarterly samples from many stream sites and seeps in the Park and by 15-minute measurements and weekly sampling at the Noland Divide watershed, which is a high elevation site sensitive to acid deposition. All samples are analyzed for pH, conductivity, acid neutralizing capacity and major anions and cations. The Noland Divide site also records flow, pH, and conductivity at 15-minute intervals in two small streams. The water quality monitoring program is integral to the Park's efforts to protect and manage its natural resources.

As part of the water quality monitoring, calcium and magnesium have been analyzed in all water samples because they are major dissolved species in the water and are important to vegetation and aquatic species. In September 1993, the previous investigators began using ion chromatography (IC) to analyze calcium and magnesium and began to realize that these analyses were suspect for several reasons including a poor ion balance. The current investigators evaluated the use of IC for calcium (Ca) and magnesium (Mg) analysis and have concluded that a different method of analysis is warranted. A search of relevant literature have shown both success and questions with using IC for Ca and Mg. Other researchers were contacted and were found to have similar problems with IC that this project experienced. The instrument manufacturer's representatives were not able to resolve the problem. Additionally, IC is not currently approved by the U.S. Environmental

Protection Agency for Ca and Mg analyses in drinking water nor is it an approved method in *Standard Methods for the Examination of Water and Wastewater*. Extensive laboratory experiments identified a serious pH effect with IC analysis of Ca and Mg that could not be overcome. For these reasons, the current investigators have decided to use the more commonly used method of atomic absorption (AA) spectrophotometry.

Archived samples for the Noland Divide streamlets were re-analyzed by AA. Regrettably, there were insufficient Park-wide samples available for meaningful re-analysis. The AA analysis of Noland Divide samples underwent rigorous quality assurance/quality control (QA/QC) procedures, and indeed the AA values for Ca and Mg brought the ion balances into line. The re-analyzed samples showed little correlation with the previous IC measured Ca and Mg. Consequently, those IC values can not be sanctioned for use except as order of magnitude values. The re-analyzed Noland Divide samples were used to construct a regression model that was used to estimate missing values of Ca and Mg for Noland Divide. These models had adjusted r-squared values of 0.66 to 0.68. Ion balances using the regression based values of Ca and Mg were also close to zero as they should be.

Time trend analyses were performed with the AA values of Ca and Mg and showed declining calcium and magnesium concentrations of from 4.7% to 16.6% over ten years for the two streamlets at Noland Divide. The reason for this decline were not the subject of this paper but may be partly due to vegetation regrowth in the watershed, which would be consistent with declines seen in nitrate, but may also be partly due to acidification processes.

Specific conclusions of the report include:

1. Poor analytical results using IC for cations in Smoky Mountains project is evidenced by poor ion balances, by apparent step increases in calcium and magnesium when IC was first implemented, and by poor results from round robin inter-laboratory comparison samples.
2. There is considerable conflicting information about whether IC is a viable choice for analysis of low concentrations of calcium and magnesium. The results of our own work, the experiences of investigators with the USGS and University of Virginia, results of Döscher et al. (1995), comments made by the instrument manufacturer's representatives and their lack of being able to identify any problem with our methods, lack of wide use of IC for cation analyses (few analytical labs use IC for this purpose) lead to a conclusion that IC is not suitable for calcium and magnesium. However, there are several papers in the literature that do report good results.
3. The experiments with IC showed significant QA/QC problems. Experiments with the method of standard additions showed that the IC measured more calcium and magnesium than what was added in the additions. Experiments also showed significant pH effects, i.e., the lower the pH of the sample, the lower the calcium or magnesium measured by the instrument. Attempts to remedy this pH effect by adjusting samples and standards to the same pH were impractical because of the weak buffering of the samples.
4. Based on the evidence and experience available and the need to move forward, the decision was made to use atomic absorption spectrophotometry for calcium and magnesium analyses. AA is widely used by analytical laboratories for these cations, and extensive QA/QC experiments on a sample Park water has shown excellent results.
5. The Pearson correlation coefficient, r_{xy} , between AA and IC measured calcium is 0.373

which is consistent with the poor results by IC. The low correlation also indicates that IC was not in error by a consistent amount or percentage. Regrettably, it must be concluded that the previous IC calcium measurements are of little value except as order of magnitude estimates. The Pearson correlation coefficient, r_{xy} , between AA and IC measured magnesium is 0.523.

6. Because flow and stream ID appear in the Noland Divide calcium and magnesium regression models as significant variables, which would not be available for Park Wide data, and because the more available chemistry data did not appear in the regression models, it was concluded that developing predictions for calcium and magnesium for Park Wide data should not be attempted.
7. Point estimates and confidence interval estimates were made for all the records used in the regression. As an indication of error, the average upper and lower 95% confidence levels for these point estimates is 6.8 $\mu\text{eq/L}$ (12.5%) for calcium and 2.29 $\mu\text{eq/L}$ (11.2%) for magnesium. This can be used as an error of the estimates for the missing calcium and magnesium values. Users are cautioned not to use the estimated values of calcium and magnesium for time trend analyses but rather should use the AA determined values of calcium and magnesium only.
8. Two different neural network software packages were used to predict calcium concentrations but did not improve the predictions enough to warrant using them.
9. The regression models using the AA values of calcium and magnesium show that calcium is decreasing by 0.913 $\mu\text{eq/L}$ and 0.281 $\mu\text{eq/L}$ per year for the southwest and northeast streamlets, respectively. This equates to a 16.6 % and a 4.7 % decrease over ten years.

Magnesium is found to decrease by 0.336 $\mu\text{eq/L}$ and 0.391 $\mu\text{eq/L}$ per year, which represents a 16.1 % and a 16.6 % decrease over ten years in the southwest and northeast streamlets, respectively. The findings of this analysis indicate significant long-term decreases and significant seasonal variations in both calcium and magnesium concentrations in stream water from the Noland Divide watershed. The reason for this decline were not the subject of this paper but may be partly due to vegetation regrowth in the watershed, which would be consistent with declines seen in nitrate, but may also be partly due to acidification processes.

Appendix A-2

Abstract of report entitled: Water Quality Characteristics, Temporal Trends, Influencing Factors for Selected Streams in the Great Smoky Mountains National Park

Data from synoptic sampling of streams in the Great Smoky Mountains (GRSM) National Park were analyzed for the years 1993-1998. The analysis was only for sites currently monitored and included 1) descriptive graphs of water quality vs elevation and maps of spatial variability, 2) relationships between drainage basin characteristics and water quality, 3) time trends, and 4) the hydrological representativeness of sampling. Historically, biannual synoptic sampling of 367 sites began in 1993. This was reduced to 160 sites in 1995 sampled monthly, and then later reduced to the current 90 sites sampled quarterly. Grab samples were taken and analyzed for major cations (calcium, magnesium, sodium, potassium and ammonium), major anions (sulfate, chloride and nitrate), pH, acid neutralization capacity (ANC), conductivity and, at times, aluminum and silica. Several purposes are served by the sampling including: long-term trend detection of impacts from acid deposition and global climate change; suitability of water quality for aquatic life; assisting the Park in managing its resources; and development of an understanding of what factors control and impact water quality.

Water Quality and Spatial Variability

Streams of the GRSM are generally low ionic strength waters (about 95% of stream sampling sites have conductivity values less than or equal to 25 microsiemens per centimeter which roughly corresponds to about 16 mg/L of total dissolved solids) with minimal ability to neutralize acids. Table 1 summarizes statistics for several water quality parameters. According to ANC classification ranges given by Webb et al. (1989) and applied to streams in the GRSM as shown in table 2, it is clear that most streams are sensitive or extremely sensitive to acid input. Also, about 77% of the sampling sites have median pH values less than 6.5, which some references cite as a concern level for effects on aquatic organisms such as sensitive benthic invertebrates and which is used as a water quality criterion in some states.

Elevation Trends

Strong elevation trends are seen for many water quality parameters. Figures 1-8 show trends for pH, ANC, nitrate, and sulfate. Other analytes are included in the body of the report. Conclusions based on these elevation trends include:

- There are no statistically significant elevation trends for chloride, conductivity, or sulfate. The lack of an elevation trend for sulfate implies that the concentration of sulfate in precipitation does not vary greatly with elevation. Indeed, the 1991-1999 average of annual mean precipitation-weighted concentrations at the Elkmont National Atmospheric Deposition Program monitoring site (Elev. 640 m) were sulfate - 1.35 mg/L (28.1 µeq/L), nitrate - 0.87 mg/L (14.1 µeq/L), ammonium - 0.16 mg/L (8.89 µeq/L), and lab

pH - 4.56 compared to the Noland Divide open site (1740 m) unweighted precipitation

Table 1. Summary statistics for different elevation classes.

Class ²	pH ¹			ANC ¹			Conductivity ¹			Nitrate ¹			Sulfate ¹		
	Mean	Median	σ	Mean	Mean	σ	Mean	Median	σ	Mean	Median	σ	Mean	Median	σ
2	6.66	6.64	0.32	145.78	102.80	140.73	23.16	19.20	12.91	10.51	7.05	9.37	44.18	40.43	12.14
3	6.57	6.47	0.40	200.95	67.08	370.11	26.94	15.10	34.33	11.50	11.26	7.56	35.63	32.78	12.86
4	6.34	6.39	0.30	59.63	59.71	38.20	13.67	13.39	2.57	12.80	8.99	11.98	32.84	28.66	17.58
5	6.30	6.35	0.30	51.62	45.77	32.30	14.82	14.36	4.13	18.79	16.64	14.60	36.77	28.75	20.19
6	6.12	6.17	0.34	30.97	26.69	23.35	14.30	13.20	4.53	23.88	23.77	13.05	42.94	36.79	24.53
7	6.18	6.17	0.28	41.47	27.27	34.82	20.41	19.15	4.57	35.23	34.85	9.99	71.19	70.67	19.49
8	5.85	5.85	0.46	22.32	17.63	40.18	20.05	19.03	8.48	34.69	36.94	17.09	74.80	65.83	55.44
9	5.74	5.95	0.68	31.62	33.99	34.23	20.84	17.35	15.20	34.58	30.52	19.96	72.80	35.69	108.9
10	5.66	5.80	0.49	18.10	18.05	15.10	17.32	16.14	4.42	49.91	47.34	13.81	37.70	28.63	17.72
11	5.11	5.05	0.38	2.14	0.34	18.22	22.85	17.65	30.24	64.31	67.41	22.52	38.04	30.57	17.92

¹ ANC, nitrate, and sulfate units are microequivalents per liter, $\mu\text{eq/L}$; conductivity is in microsiemens per centimeter.

² Elevation classes in meters are 2: 305-457, 3: 457-610, 4: 610-762, 5: 762-914, 6: 914-1,067, 7: 1,067-1,219, 8: 1,219-1,372, 9: 1,372-1,524, 10: 1,524-1,676, 11: >1676.

Table 2. Summary of acidic level of water at sampled sites.

ANC range ($\mu\text{eq/L}$)	Classification	Percentage of sample sites with median ANC within range
< 0	acidic	4 to 5
0 - 50	extremely sensitive	52
50 - 200	sensitive	40
> 200	not classified	3

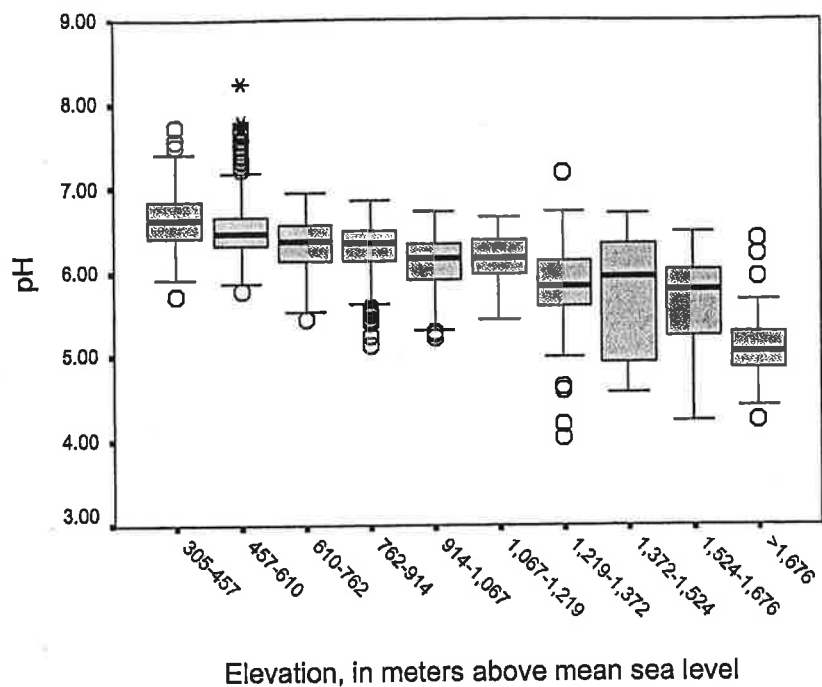


Figure 1. Elevation trend for pH in sampled GRSM streams.

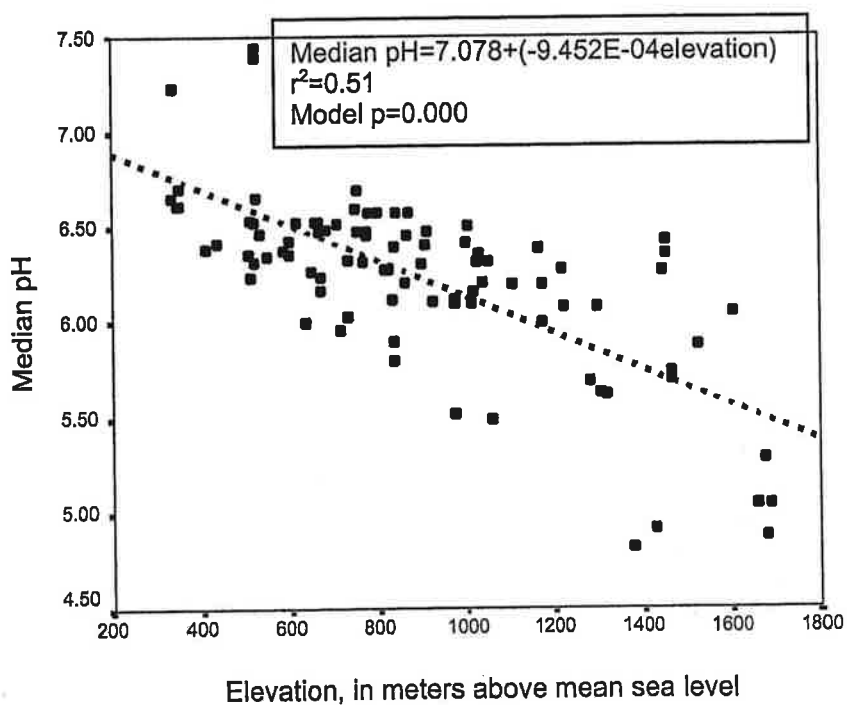


Figure 2. Regression analysis of median pH in sampled GRSM streams.

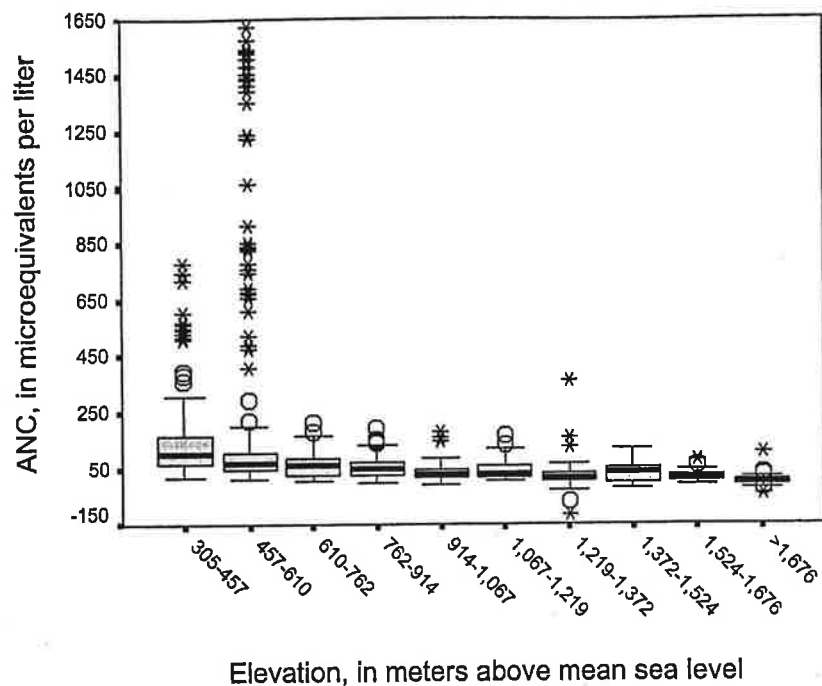


Figure 3. Variability of acid neutralizing capacity in sampled GRSM streams.

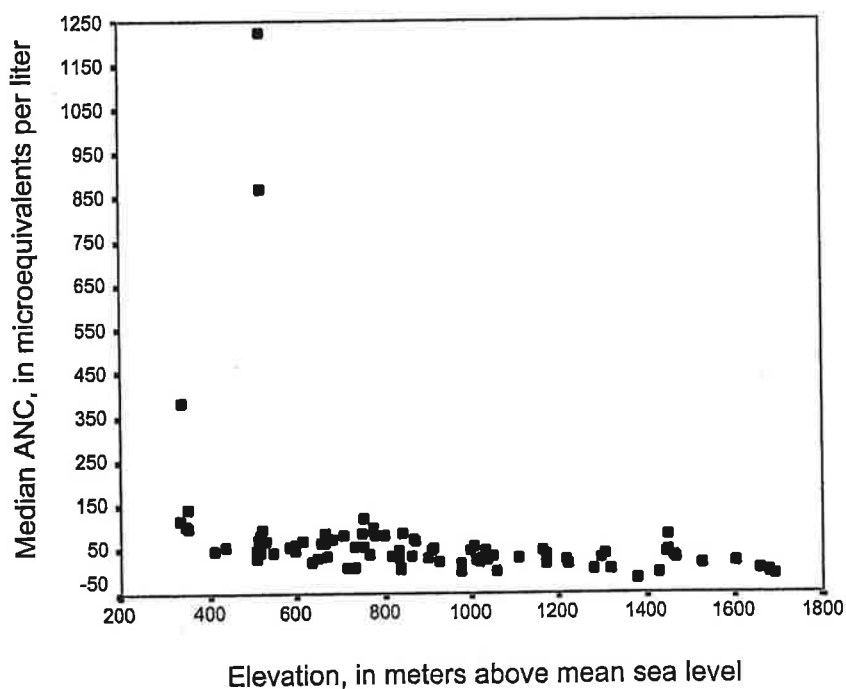


Figure 4. Scatter plot of median acid neutralizing capacity in sampled GRSM streams.

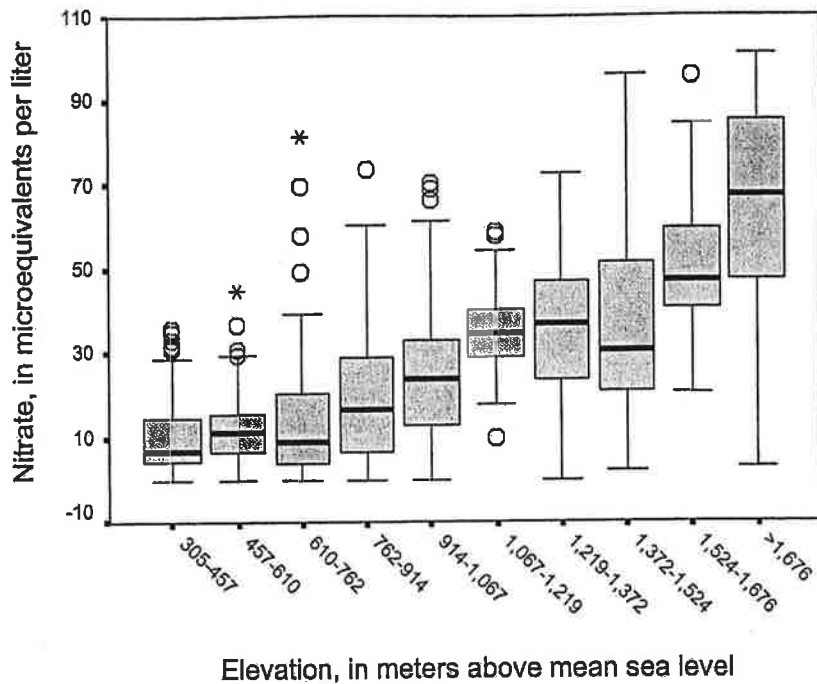


Figure 5. Elevation trend for nitrate in sampled GRSM streams.

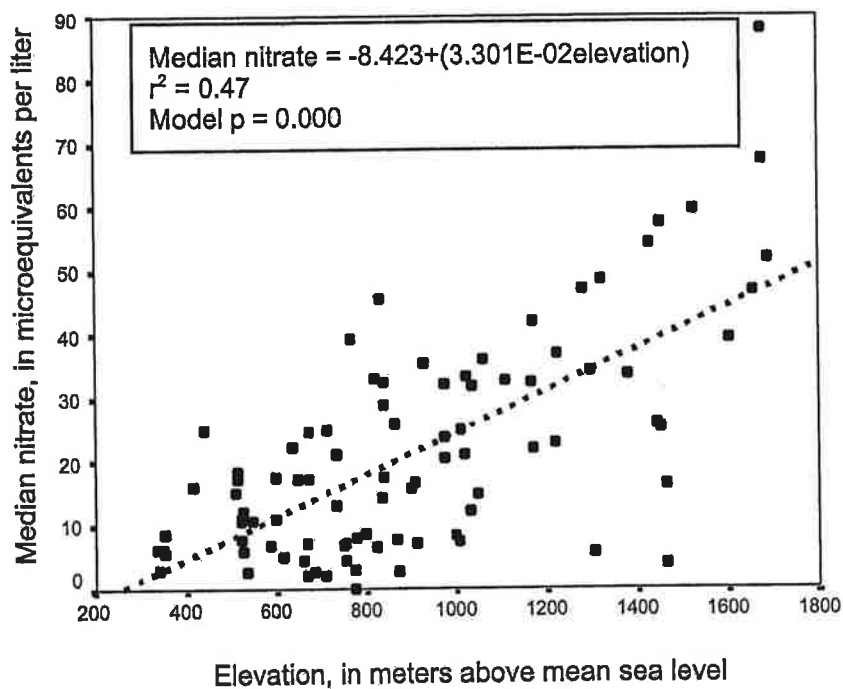


Figure 6. Regression analysis of median nitrate in sampled GRSM streams.

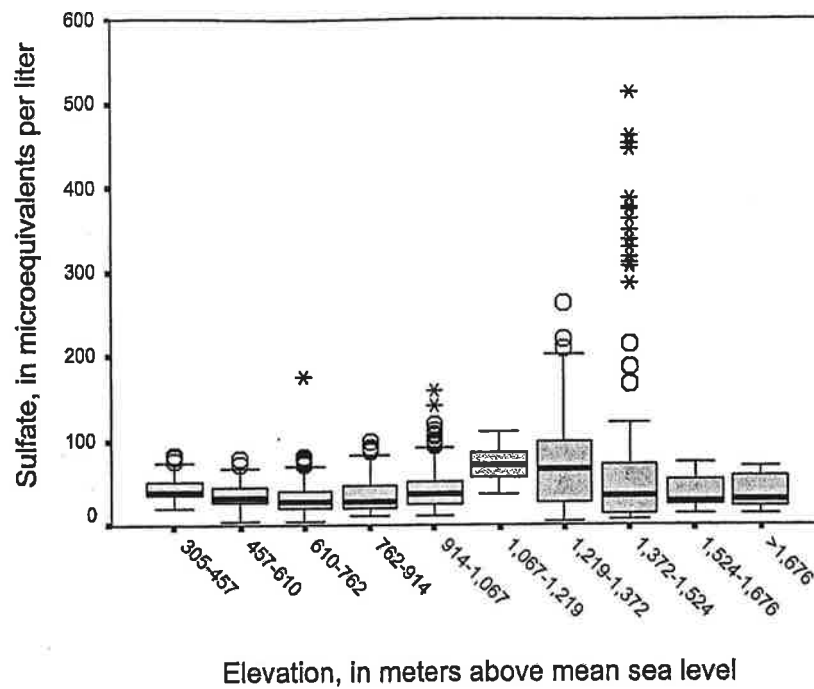


Figure 7. Variability of sulfate in sampled GRSM streams.

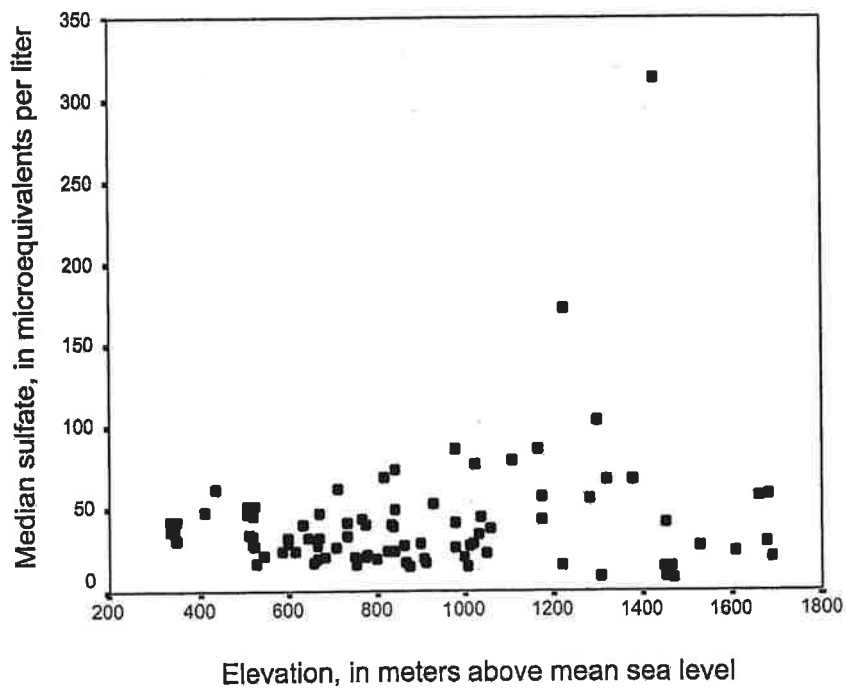


Figure 8. Scatter plot of median sulfate in sampled GRSM streams.

ns of sulfate - 1.67 mg/L (34.8 μ eq/L), nitrate - 0.87 mg/L (14.1 μ eq/L), ammonium - 0.27 mg/L (14.73 μ eq/L), and lab pH - 4.62. All things considered, sulfate, nitrate, and pH are similar between the two sites but ammonium differs by about a factor of 2. (Note that similar sulfate concentrations do not contradict a much greater flux of sulfate at higher elevations. A greater flux at higher elevations is expected, because there is greater precipitation at higher elevations. It also does not in any way imply that stream acidification is not caused by acid deposition.) For most elevation classes shown in table 1, the sulfate concentration in the precipitation approximates the stream concentration. It should also be noted that there is a peak in sulfate concentration in the 1000-1500 m elevation range most likely due to sulfate bearing geologies which is then diluted at lower elevations. The lack of an elevational change in conductivity, which is an aggregate measure of total ion concentration, implies that there is not a very large change in the total concentration of ions but does not rule out changes in ionic composition.

- There is a statistically significant increase in nitrate and decrease in sodium and potassium as elevation increases. ANC also decreases as elevation increases, and ANC concentrations are more variable at lower elevation due to presence of carbonate geologies. (Note that ANC is closely tied to bicarbonate concentration which is presumed to be the dominant alkalinity form: $[\text{HCO}_3^-] = \text{ANC} + [\text{H}^+]$.) The reason for the increase in nitrate with higher elevation could result from higher concentrations in precipitation or greater fluxes at higher elevations, interactions with soil, e.g., nitrate saturation of the soil at high elevations, uptake/release of nitrate by vegetation, which concurrently releases alkalinity, or a combination of these or other mechanisms. According to some experts, it is reasonable to expect lower nitrate concentrations at lower elevations because of greater nitrogen uptake at lower elevations due to younger forests, however no direct quantitative proof of this effect can be offered at this time. It is noted that the sum of ammonia, which should oxidize to nitrate, and nitrate concentrations in precipitation is 29 μ eq/L at Noland Divide compared to 23 μ eq/L at Elkmont. Table 1 shows that nitrate concentrations in lower elevation streams are less than the precipitation values while higher elevation streams and springs exceed them. It is also noted that the decrease in nitrate from high elevations to low is on the same order of magnitude as the increase in bicarbonate as seen in table 3.
- There is a statistically significant trend of decreasing pH with increasing elevation. The median pH is 5.05 for the highest elevation class and 6.64 for the lowest. The mechanisms driving the pH elevational gradient have not been established with certainty. Based on earlier discussions of sulfate trends, it does not seem likely that pH elevational gradients are strongly linked to elevational gradients in the concentration of sulfate or nitrate in precipitation. There may be a relationship with flux rates, but it seems more plausible that the pH change is related to chemical/biochemical reactions in the watersheds which change the overall ionic composition. It is noted that there is a statistically significant correlation between pH and ANC, nitrate, sulfate, sodium, and potassium with Kendall's tau correlation coefficients of 0.869, -0.588, -0.309, 0.589 and 0.494 respectively. In other

Table 3. Changes in ion concentrations with elevation.

Constituent	Change in ions, $\mu\text{eq/L}$ (Highest elevation class - lowest) ¹	Change in ion, $\mu\text{eq/L}$ (Third highest elevation class - lowest) ¹
CATIONS		
H ⁺	- 8	-1
Na ⁺	+14	+10
K ⁺	+1	+2
Ca ²⁺	not available	not available
Mg ²⁺	not available	not available
TOTAL CHANGE	+10	+11
ANIONS		
HCO ₃ ⁻ (without ANC outlier)	+89	+79
NO ₃ ⁻	-61	-29
Cl ⁻	0	-1
SO ₄ ²⁻	+13	-20
TOTAL CHANGE	+41	+29

¹The highest elevation class has only spring sources and the third highest class is the highest elevation class not strongly influenced by springs.

words, as pH increases, i.e., as the proton concentration decreases, the sodium, potassium and calculated bicarbonate concentrations increase while the sulfate and nitrate concentrations decrease. This would be consistent with chemical/biochemical reactions which are substituting the hydrogen ion with other cations. Regrettably, valid calcium and magnesium data are not available for this period, but future analyses incorporating such data may provide further insights. Note that the actual change in hydrogen ion concentration is for the most part much smaller than the change in total cation or total anion concentrations as shown in table 3. The correlation between pH and sulfate, which is the weakest of the above, is most likely due to sulfide bearing geologies. A clear correlation of lower pH with pine and fir forests compared to hardwood was expected but not seen.

Relationships Between Watershed Characteristics and Water Quality

An understanding was sought of what factors control water quality in the Park. The specific objective was to identify relationships between the water quality at the sampling sites and the characteristics of the contributing drainage basin. Correlation analysis and multiple linear regression were the tools used to uncover relationships. The drainage basin characteristics included geophysical descriptors (basin coordinates, azimuth, elevation, slope, length, area, and shape), hydrologic descriptors (stream order, stream density, channel slope, and maximum channel length), the percentage of basin underlain by various bedrock geological formations, the percentage of basin covered by various forest types or balds, and the percentage of basin having been undisturbed, lightly cut, selectively cut, heavily cut, or settled. Through correlation analyses, discussion with experts, and trial regressions, the independent variables, i.e., the drainage basin characteristics, were reduced to a more manageable number by combining several similar geologies and by eliminating variables that were highly correlated with each other. Notably, the orientation, i.e., azimuth of the basin's axis, did not show significant correlation with water quality, and was not considered further.

The multiple regression method used to identify statistically significant relationships was a rigorous step-wise multiple linear regression procedure using SPSS. The details of the procedure are documented in the report, but included minimization of collinearity, analysis of the influence of outliers, and inspection of partial regression plots for problems such as curvature and heteroscedasticity which if found led to investigation of data transformations to find the best model.

The results of the regressions are summarized in tables 4 and 5. Several observations and conclusions are summarized below:

- The regression models fit the data well and explained much of the variance in the data in several cases. For all the models, the adjusted r-square ranged from 0.55 to 0.98.
- The presence of limestone or Anakeesta formations in a watershed significantly effects

Table 4. Summary of stepwise regression results for predicting median water quality constituent values using basin characteristics.

Constituent	Model	Adjusted r ²	Model p
pH	$7.821 + (-5.806E-04 \bullet \text{mean elevation in meters}) + (-2.203E-02 \bullet \text{basin slope in percent}) + (8.829-02 \bullet \text{stream order})$	0.74	0.000
ANC ^a	61.602•%Limestone	0.98	0.000
ANC ^b	$52.976 + (0.863 \bullet \%MMMTPXPXPO) + (8.603 \bullet (\text{max channel length in kilometers})^{0.5}) + (-1.089 \bullet \text{basin slope in percent})$	0.81	0.000
Conductivity ^a	12.974+(5.538•%Limestone)	0.98	0.000
Conductivity ^b	$11.914 + (4.526E-02 \bullet \%undisturbed) + (3.446E-02 \bullet \%Anakeesta)$	0.55	0.000
Nitrate	$7.651 + (0.222 \bullet \%undisturbed) + (2.689 \bullet \text{elevation class}) + (-5.190 \bullet \text{stream density in kilometers per square kilometer}) + (-0.238 \bullet \%MMH) + (-5.555E-02 \bullet \%Anakeesta)$	0.87	0.000
Sulfate	$21.320 + (2.997E-03 \bullet (\%undisturbed)^2) + (1.922 \bullet (\%Anakeesta)^{0.5})$	0.63	0.000
Chloride	$14.901 + (-1.143 \bullet \text{stream density in kilometers per square kilometer}) + (0.394 \bullet \%Limestone) + (2.156E-02 \bullet \%Elkmont Sandstone) + (2.635E-02 \bullet \%Northern Hardwood)$	0.60	0.000
Sodium ^a	44.926+(9.377•log(%Limestone))	0.88	0.003
Sodium ^b	$54.116 + (-0.508 \bullet \text{basin slope in percent}) + (0.494 \bullet \%MMH)$	0.71	0.000
Potassium	$19.842 + (-0.169 \bullet \text{basin slope in percent}) + (-4.581E-02 \bullet \%Anakeesta) + (-4.266E-02 \bullet \%Northern Hardwood)$	0.70	0.000

Note: All coefficients and constants reported are significant (p<0.10). MMH is the percentage of the basin covered by Mixed Mesic Hardwood.

MMMTPXPXPO is the percentage of the basin covered by Mesic Oak, Mixed Mesic Hardwood, Tulip Poplar, Pine, Xeric Oak, and Pine-Oak.

^ais the regression equation for basins which contain Limestone.

^bis the regression equation for basins which have no Limestone.

Table 5. Water quality constituent model application information.

Model	Predicted (min, max, median) ^{1,2}	Observed (min, max, median) ^{2,3}	Independent variable ranges Independent variable (min, max) ^{1,4}	Model restrictions and applicability
pH	(5.62, 7.09, 6.36)	(5.49, 7.44, 6.36)	mean elevation (745, 1,716) basin slope (25.3, 72.1) stream order (1, 5)	Independent variables should be within ranges listed Not applicable for basins with disturbed Anakeesta
ANC ^a	(24.02, 1,295.49, 285.22)	(95.89, 1,223.05, 265.50)	Limestone (0.4, 21.0)	Independent variable should be within range listed Applicable for basins which contain Limestone and no disturbed Anakeesta
ANC ^b	(-1.25, 103.12, 43.07)	(-13.68, 124.27, 44.63)	MMTPXPO (0.0, 72.1) max channel length (0.52, 41.62) basin slope (25.3, 72.1)	Independent variables should be within ranges listed Applicable for basins without Limestone and no disturbed Anakeesta
Conductivity ^a	(15.13, 129.43, 38.61)	(17.58, 126.40, 33.98)	Limestone (0.4, 21.0)	Independent variable should be within range listed Applicable for basins which contain Limestone and no disturbed Anakeesta
Conductivity ^b	(11.91, 19.89, 14.87)	(10.42, 24.30, 13.90)	undisturbed (0.0, 100.0) Anakeesta (0.0, 100.0)	Independent variables should be within ranges listed Applicable for basins without Limestone and no disturbed Anakeesta
Nitrate	(0.57, 51.16, 19.00)	(3.07, 59.69, 17.62)	undisturbed (0.0, 100.0) elevation class (2, 10) stream density (0.1, 2.4) MMH (0.0, 34.9) Anakeesta (0.0, 100.0)	Independent variables should be within ranges listed No other restrictions
Sulfate	(21.32, 70.51, 34.42)	(9.07, 104.88, 32.72)	undisturbed (0.0, 100.0) Anakeesta (0.0, 100.0)	Independent variables should be within ranges listed Not applicable for basins with disturbed Anakeesta
Chloride	(12.53, 22.04, 13.73)	(11.49, 20.71, 13.78)	stream density (0.1, 2.4) Limestone (0.0, 21.0) Elkmont Sandstone (0.0, 93.4) Northern Hardwood (0.0, 58.5)	Independent variables should be within ranges listed No other restrictions
Sodium ^a	(41.09, 57.33, 50.58)	(41.20, 56.02, 52.21)	Limestone (0.4, 21.0)	Independent variable should be within range listed Applicable for basins which contain Limestone and no disturbed Anakeesta
Sodium ^b	(20.22, 56.47, 33.76)	(21.96, 69.58, 35.04)	basin slope (25.3, 72.1) MMH (0.0, 49.3)	Independent variables should be within ranges listed Applicable for basins without Limestone and no disturbed Anakeesta
Potassium	(2.82, 14.35, 10.30)	(3.17, 16.78, 10.29)	basin slope (25.3, 72.1) Anakeesta (0.0, 100.0) Northern Hardwood (0.0, 58.5)	Independent variables should be within ranges listed No other restrictions

¹Predicted column includes summary statistics for model predicted values.²Observed column includes summary statistics of dependent variable in basins used for model development.³Units for all water quality constituents are microequivalents per liter except pH (standard units) and conductivity (microsiemens per centimeter).⁴For explanation of abbreviated independent variables, see bottom of Table 3-4 in report.

water quality. Disturbed Anakeesta effects water quality much more than undisturbed, but it was not possible to develop models specific to disturbed Anakeesta areas due to a paucity of data.

- The regression model for pH has an adjusted r-square of 0.74 and figure 9 shows a good fit of predicted vs actual values. The predictor variables were elevation, basin slope and stream order, all of which have some relation to elevation but not enough to drop them from the model because of collinearity problems. Interestingly, the percentage of undisturbed Anakeesta in the watershed was not a significant variable, but the model is not valid for disturbed Anakeesta.
- ANC required separate regression models for presence or absence of limestone. The model for when limestone is present is a near perfect linear relationship between the percentage of limestone in basin and ANC and has an adjusted r-square of 0.98.
- The regression model for nitrate has an adjusted r-square of 0.87. The model reflects a strong elevation gradient as discussed earlier, i.e., increased nitrate with higher elevation. Nitrate also increases with the percentage of basin undisturbed. This is consistent with undisturbed areas generally being older forests with lower nitrogen uptake needs. Disturbed areas presumably have younger, faster growing vegetation that take up more nitrate. Mixed Mesic Hardwood is another significant variable in the model which may be a surrogate for disturbance because these forests are at lower elevations that were previously logged or settled.
- The regression model for sulfate has an adjusted r-square of 0.63. The model shows a strong Anakeesta influence. The percentage of Anakeesta in watersheds ranges from 0 to 100%, and the model thus predicts a sulfate increase of 19.2 $\mu\text{eq/L}$ in going from 0% to 100%, or approximately double the sulfate concentration of a basin without Anakeesta. Elevation was not significant predictor of sulfate concentration.

Temporal Variability

An important part of this work was to evaluate seasonal differences in water quality and to identify long term time trends. Seasonal differences were statistically tested using the Kruskal Wallis H test. Time trends were identified by using multiple linear regression which included sine and cosine terms to model seasonality. Time trend regressions used water quality values that were normalized to the mean of each sampling site in order to make the data more consistent. The form of the regression model was:

$$(\text{normalized concentration}) = a + b \cdot \cos\theta + c \cdot \sin\theta + d \cdot t$$

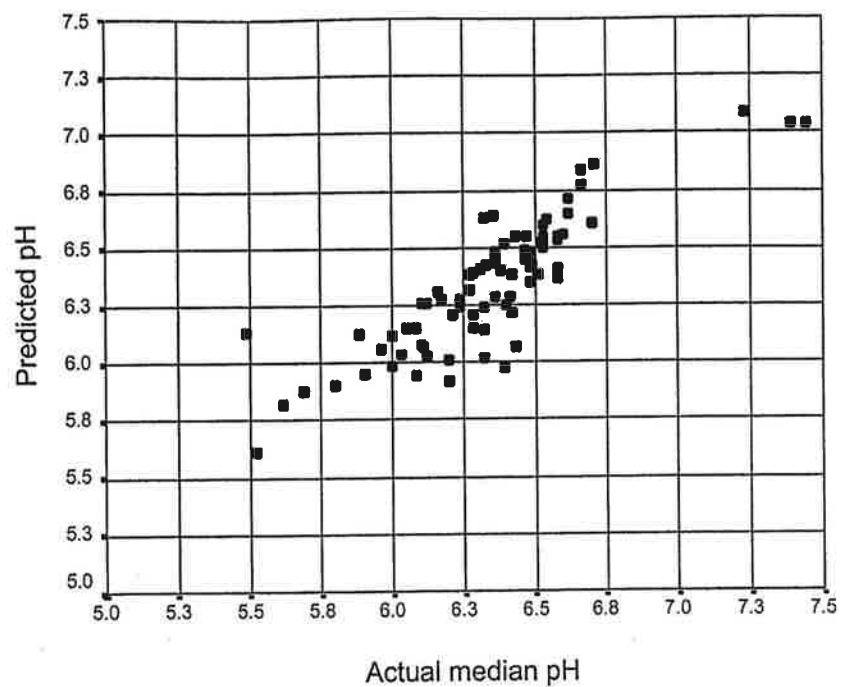


Figure 9. Predicted versus actual pH from regression model to predict pH in sampled GRSM basins.

where:

(normalized concentration) = predicted normalized concentration at any time, t

$\theta = 2\pi \cdot (\text{fraction of a year})$

t = cumulative Julian days

The results of tests for seasonal differences show that the highest concentrations of most water quality parameters generally occur in the late fall sampling period and lowest concentrations occur in the winter sampling period. A notable exception is nitrate which sees lowest concentration in late fall, whose samples were often taken near the end of the growing season, and highest concentrations in winter probably due to leaf decay and cessation of the growing season.

Regression models for time trends were constructed for each water quality parameter and for each elevation class. Table 6 and figure 10 show examples of the time trend studies. Some elevation classes show statistically significant long term time trends for nitrate, pH, and hydrogen ion concentration, but ANC, conductivity, sulfate generally did not show long term time trends.

Long term time trends for pH are of particular concern because of potential impacts on stream ecological health. The five elevation classes from 305 to 1067 m and class 10 from 1524-1676 m show statistically significant time trends. The other elevation classes did not show time trends, at least at the 95% confidence level. For the elevation classes showing time trends, the r-square ranged from 0.044 to 0.232. These are not high r-square values and the tendency might be to discount the regressions because much of the variability is unexplained. But the fact remains that the time trends are statistically significant at the 95% confidence level and do raise some cause for concern especially since the trends are consistent with acidification problems in the Eastern U.S.

By using the time trends identified through regression, the time to reach critical pH values can be projected for the different elevation classes. In making these projections it must be clearly understood that this assumes that the present statistically identified trends continue, that conditions remain the same, that there are no reductions in atmospheric emissions of pollutants, and that there are no ameliorating chemical or biochemical processes. Bearing this in mind, the times to reach several critical pH levels are shown in table 7. The table raises issues which further research will try to clarify as more sampling data becomes available. It is also not clear why ANC does not show a time trend whereas pH and proton do.

Sampling of Extreme Events

The current Park wide sampling strategy does a good job of characterizing base line or average water quality conditions. However, the sampling program was not designed to sample extreme events such as storm events. Sampling storm events is important because the worst water quality and highest contaminant fluxes should occur during storms when accumulated contaminants are flushed from the basin into the streams. Limited previous storm event

sampling

Table 6. Time trend analysis of normalized pH.

Elevation class	Model	r²	Model p
2	normalized pH=1.017+(-1.899E-02)•cosθ+(-1.262E-02)•sinθ+(-1.008E-05)•t	0.214	0.000
3	normalized pH=1.032+(-1.167E-02)•cosθ+(-6.695E-03)•sinθ+(-1.580E-05)•t	0.099	0.000
4	normalized pH=1.025+(-1.210E-05)•t	0.044	0.000
5	normalized pH=1.024+(-8.517E-03)•cosθ+(-7.697E-03)•sinθ+(-1.385E-05)•t	0.103	0.000
6	normalized pH=1.036+(-9.153E-03)•cosθ+(-1.498E-02)•sinθ+(-2.016E-05)t	0.232	0.000
7	normalized pH=0.996+(-8.964E-03)•cosθ+(-2.321E-02)•sinθ	0.262	0.000
8		0.032	0.225
9	normalized pH=1.014+(-2.020E-02)•cosθ+(-8.178E-03)•sinθ	0.030	0.105
10	normalized pH=1.071+(-3.561E-05)•t	0.132	0.002
11		0.041	0.487

Note: Shaded regions denote all independent variables were insignificant (p>0.10).

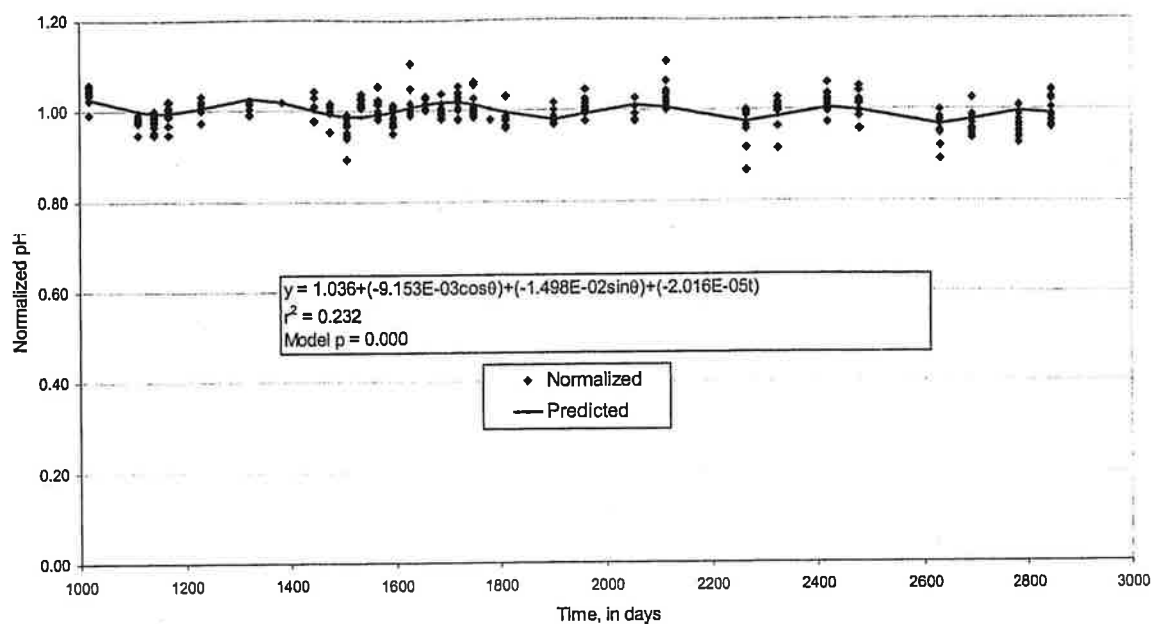


Figure 10. Time trend for pH withing elevation class 6 (914-1,067).

Table 7. Summary of time to critical pH values within the elevation classes.

Class	Median pH	% annual decrease in normalized pH	t to 6.50	t to 6.00	t to 5.50	t to 5.00
2	6.64	0.37	6	26	46	67
3	6.47	0.58		13	26	39
4	6.39	0.44		14	32	50
5	6.35	0.51		11	26	42
6	6.17	0.74		4	15	26
7	6.17					
8	5.85					
9	5.95					
10	5.80	1.30			4	11
11	5.05					

Note: Time (t) to critical pH values is in years. Shaded regions indicate no significant trend.

has shown much higher aluminum and much lower pH during storm flows. The current study quantitatively evaluated how well the frequency of sampling represented the frequency of flow rates as represented by records for Little R and Cataloochee Creek. The results indicate that indeed the current sampling program does a good job of sampling average conditions but seriously under-represents sampling of high flows.

Importance of Work

The results of this work has several implications to Park management and future water quality research:

- The greatest concern is the long term water quality in the Great Smoky Mountains National Park. Of the water quality parameters measured, pH is the greatest water quality concern. The statistically significant decline in pH is clearly the wrong direction and affirms the need for continued long term monitoring as well as analysis of more recent data. Further research is also desired to explain more of the variability in the pH time trend regressions. This includes incorporating other variables such as recently available calcium and magnesium data, future soil survey results, and precipitation data which were not able to be included for various reasons. The analyses presented herein also points out the need for continued collection of precipitation data to fully understand water quality trends both temporally and spatially. Finally, past practice in monitoring programs at National Parks including the GRSM appears to have been to measure pH in the lab rather than the field. Recognized methodologies that the authors are aware of require field pH values in order to avoid pH drift due to carbon dioxide exchange. Field pH measurement needs to be implemented as soon as practical and comparisons made between field and lab values.
- The results help to understand the state of and trends in water quality in the GRSM, what controls water quality, and how it may be changing as summarized above. The results raise many questions and mark directions for future research. Particularly important is to more fully link the results of this work with other work ongoing inside and outside the GRSM.
- The results of these analyses confirm that storm events are under-represented. Thus, very little information is being collected during the worst water quality conditions.
- The results also confirm what management already knows about the impact of Anakeesta disturbances on pH but also shows that undisturbed areas do not have statistically identifiable impact on pH. The results also show that the percentage of limestone in a basin is linearly related to ANC and can help identify some areas that should not be sensitive to acid input.
- The results of this work will also help in the ongoing process of evaluating the current sampling network and deciding which sites can be eliminated with no significant loss in

statistical resolution.

