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I am submitting herewith a thesis written by Tim Pobst entitled "Statistical Temporal Analyses on Legacy Data for the GRSM Stream Survey." I have examined the final paper copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

We have read this thesis and recommend its acceptance:	Dr. John Schwartz, Major Professor
Dr. Bruce Robinson	_
Dr. Qiang He	_
	Accepted for the Council:
	Carolyn R. Hodges  Vice Proyect and Deep of the Craduate School

To the Graduate Council:

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Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

# Statistical Temporal Analyses on Legacy Data for the GRSM Stream Survey

A Thesis Presented for

The Master of Science

Degree

The University of Tennessee, Knoxville

Tim Pobst

May 2014

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### Abstract

The upper elevations of the GRSM receive some of the highest loading rates of acidifying nitrogen and sulfur species in North America (Johnson et al., 1992). Acid deposition will acidify the surface waters, which can harm anything that interacts with it, including the soils, life forms and streams. The Great Smoky Mountains National Park (GRSM) is located in the southern Appalachians spanning eastern Tennessee and western North Carolina. The GRSM is one the most visited parks in the U.S. and its conservation is a high priority for the National Park Services (NPS) which is tasked with preserving it. Park conservation is ever changing and includes monitoring streams for the consequences of acid deposition. Stream grab samples from the park have been collected and studied under the park-wide stream survey program since 1993. Stream health is determined by statistical analysis on water quality constituents such as pH, Acid Neutralizing Capacity (ANC), Nitrate, and Sulfate. In 2002 Robinson et al. (2008) found negative pH time trends, while more recently John S. Schwartz (2014) reports increasing pH trends. This paper will reproduce trends from the previous studies while adding trends from more recent data. Along with the inflection of pH trends found by John S. Schwartz (2014) a pattern of decreasing sulfate concentrations found in the high elevation site Noland Divide may correspond to the recent decrease of sulfur dioxide emissions of the Kingston and Bull run power plants. This may be studied by time trends, but a Bonferroni means comparison is used to further study the apparent correlation. Currently elevation in the survey is characterized through the use of elevation bands of which the sites belong to. This is done to focus on the strong elevation trends of many of the water quality constituents. There is concern for the survey's lack of high elevation sites, where the park is affected by acid deposition the most (Weathers et al., 2006). This paper re-draws the boundaries of the elevation bands from eleven down to six in an attempt to strengthen the upper elevations. A power analysis is then conducted to determine the inherent power of the bands to accurately report a time trend.

These analysis reported healthy streams with a continuing increase of pH and ANC trends while both the studied pollutants  $NO_3^-$  and  $SO_4^{2-}$  are decreasing. The concerns of lowering pH raised in Robinson et al. (2008) are now not as important as those for  $SO_4^{2-}$  desorption raised in John S. Schwartz (2014). The lack of elevation trend in  $SO_4^{2-}$  was attributed to high elevation soil adsorption of depositional  $SO_4^{2-}$ and a statement was made that  $SO_4^{2-}$  remains absorbed to soil particles as long as soil water chemistry remains high in SO<sub>4</sub><sup>2-</sup> concentration and low in pH (Cai et al., 2011). The slope for the elevation trend of  $SO_4^{2-}$  over the three sets is decreasing but most of the mean  $SO_4^{2-}$  concentrations listed in Appendix B are increasing through time along with pH. This suggests desorption of  $SO_4^{2-}$  into the streams, thus raising the lower elevation  $SO_4^{2-}$  concentrations up to the higher concentrations of upper elevation sites. The Bonferroni analysis found no obvious connection between the decreases in power plant emissions and sulfate concentrations in the park. It is possible that further study could produce more positive results of a delayed reaction from emissions to stream concentrations. A post-hoc power analysis found all of the trends from the time trend analysis to be overpowered, this is probably due to the large datasets used. While the a priori power analysis suggests about 110 observations are required for a trend to receive a power of .80. This result is further manipulated to show how the sites in the Stream Survey may be re-organized for a more even elevational distribution of sites.

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# Chapter 1

# Introduction

#### 1.1 Description of Study Area

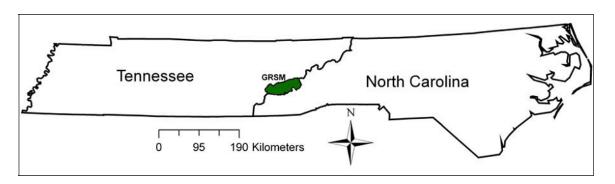


Figure 1.1: Location of the Great Smoky Mountain National Park

The Great Smoky Mountains National Park (GRSM), which is located in the southern Appalachians spanning eastern Tennessee and western North Carolina, is the second largest national park in the eastern United States. It contains roughly 100 species of native trees, more than 1,500 flowering plants, 200 species of birds, 66 types of mammals, 50 native fishes, 39 kinds of reptiles, and 43 species of amphibians. The unique nature of the park has earned it the title of International Biosphere Reserve by the United Nations (NPS, 2013). Partly due to this diversity of life, the GRSM is one the most visited parks in the U.S. and its conservation is a high priority for the National Park Services (NPS) which is tasked with preserving it. Park conservation

is constantly changing and includes monitoring streams for the consequences of acid deposition.

#### 1.2 Acid Deposition and the GRSM

Acid deposition is characterized as wet deposition (rain and snow), dry deposition (gases and particles), and fog or cloud deposition (occult) (Lovett, 1994). These three modes of pollutant transportation, transport and deposit acid pollution over the industrialized world (Board et al., 1983). The dominant man-made source of acid deposition is fossil fuel combustion, such as gas engines for transportation, and industrial plants for production and power (EPA, 2012). Power plants expel sulfur oxides ( $SO_x$ ) and nitrogen oxides ( $NO_x$ ) high into the atmosphere through smoke stacks where they react and fall to the earth as acid deposition. Once the pollutants have entered the environment they react with hydroxide and oxygen in the air, the surface waters, the soil, and on man-made structures to produce acids (Board et al., 1983).

The upper elevations of the GRSM receive some of the highest loading rates of acidifying nitrogen and sulfur species in North America (Johnson et al., 1992; Weathers et al., 2006). Acid deposition will acidify surface waters, potentially harming aquatic biota (Neff et al., 2009). The rate of stream acidification is related to both the concentration of ANC (acid neutralizing capacity) and base cations present in the stream. ANC can decrease along with stream pH partly due to base cation depletion, which can occur through leaching, another cause of increased acid input. In this process, the inherent base cation minerals react and run out leaving excess H<sup>+</sup> and Al to be released into the water (Sullivan et al., 2004). The increased H<sup>+</sup> concentration will lower the pH and the presence of Al can be toxic to fish (Driscoll et al., 2003). A constant removal of base cations can lead to permanent ANC values less than zero or chronic acidification.

Acidification of water bodies can be either chronic or episodic. Chronic acidification occurs when the body of water has constant low ANC, which creates a large area of almost un-inhabitable water where aquatic life would struggle to survive. Episodic acidification describes a rapid increase of acidity due to large surges of pollutants, usually from snow melts or heavy rains. While chronic acidification may inhibit habitation, episodic acidification can kill aquatic life by quickly dropping the pH of streams, not allowing for adaptation or moving (Sullivan et al., 2004). A literature review in Neff et al. (2009) approximates a pH of 6 for negative biological effects and a pH of 5 for mortality for trout in the park. Stream pH levels between 5 and 6 can become toxic in the presence of aluminum through leaching and base cation exchange. This toxicity can be harmful to eggs and fry in very soft waters in the lower end of the range.

#### 1.3 The Park-Wide Stream Survey

The park-wide stream survey began as part of the park's Inventory and Monitoring program of the GRSM in 1993 in response to acidification of the parks streams (Harwell, 2001). Currently grab samples are collected six times per year from 32 sites in five watersheds (Abrams, Cataloochee, Cosby, Little, Oconaluftee) and twice a year from 11 sites in Hazel Creek in order to monitor the health of the park's streams. Historically there were nearly 390 sites listed in the stream survey, but over time the number of sites monitored has been reduced to the 43 sites used in this study. Every sample is measured for pH, ANC, conductivity, acid anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, ammonium (NH<sub>4</sub><sup>+</sup>)), the base cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>), and dissolved metals (Al, Cu, Fe, Mn, Si and Zn). A ManTech<sup>TM</sup> autotitrator was used for pH, ANC, and conductivity. A Dionex<sup>TM</sup> ion chromatograph (IC) was used for the analysis of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup>. A Thermo-Scientific<sup>TM</sup> Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) was used for the study of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Al, Cu, Fe, Mn, Si and Zn.

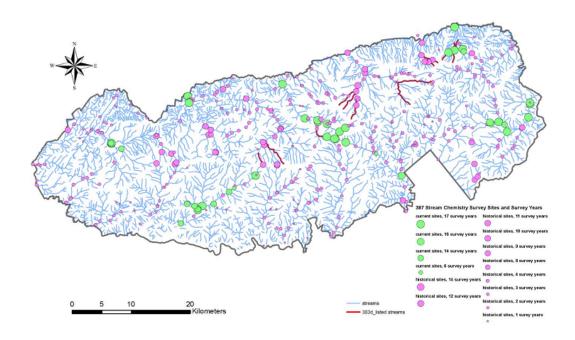


Figure 1.2: Site locations for the Stream Survey from 1993 to 2009.

All data is collected, under contract, for the NPS. Study site identifiers such as time, place, water temperature, and weather are recorded on site for each sample. This data goes all the way back to the beginning of the survey in 1993. Along with specific sample measurements, each sample is labeled by its site ID, which indicates the location. Several important characteristics are known for each site, such as stream name, geology, and elevation. All of these are used to study acid deposition in the GRSM. In 2003, the survey was improved by carefully decreasing the number of sites from 90 to the current 43 (Odom, 2003). Discontinuation of sites periodically throughout the years has created a non-uniform database making statistical analysis problematic. Along with different sites for different years, the base flow/storm flow classification is also inconsistent. The data is labeled base flow/storm flow beginning

in 1993 and ending in 2010, while data up to 2012 will be analyzed here. Two years of sample data are missing this classification.

#### 1.3.1 Elevation Bands

Elevation and basin location, are some of the more important characteristics governing water chemistry of each site location (Neff et al., 2012). Elevation was found to be a dominant driver for predicting water quality among the park's streams. Many of the water quality variables can be characterized by elevation: pH, ANC, the acid anions, and the base cations. Overall, results from the Biotics Effects report found that stream pH and ANC decreased at -.32 units and -35.73  $\mu eqL^{-1}$ respectively, per 1,000-ft elevation gain (John S. Schwartz, 2014). Many factors affect the pH of mountain streams, but clouds affect higher elevations more than they affect lower elevations, sometimes accounting for lower pH values in the higher elevations (Shubzda et al., 1995). The correlation between pH and elevation is studied in the park by the use elevation bands. Conductivity, Cl<sup>-</sup>, and base cations were also found to be correlated to elevation by significantly decreasing as elevation increases.  $SO_4^{-2}$  showed no significant trend with elevation, however  $NO_3^-$  was found to significantly increase with elevation gain. The GRSM 2011 Annual Water Quality Report compared pH trend lines representing the current 43 sites from 1993 through 2010 (UTK, 2012). The data showed lines of similar slopes with different intercepts, which was interpreted to mean increasing pH at all elevations in GRSM streams. The elevation bands are also useful because higher elevations experience increased  $SO_4^{-2}$  and prolonged acidification if soil desorption becomes a dominant geochemical watershed process, which could occur if pH increased to 6.0 and  $\mathrm{SO_4^{-2}}$  dropped below 50 eq L-1 (UTK, 2012). From a management perspective, John S. Schwartz (2014) describes potential limitations in the data to assess long-term changes in stream water quality because locations sampled have changed over time and most of the current sample locations are at lower elevations.

Elevation class	Range of elevation (ft) MSL	Number of sampling sites	Percent of NPS area*	Percent of sampling sites
1	<1000	0		
2	1000-1500	7		
3	1500-2000	13	43.3	65.0
4	2000-2500	16		
5	2500-3000	18		
6	3000-3500	13	27.4	20.5
7	3500-4000	4		
8	4000-4500	5	21.2	12.1
9	4500-5000	5		
10	5000-5500	1	8.1	2.4
11	>5500	1		

**Table 1.1:** Historical elevation bands for the 90 site survey. \*Approximate percentages based on planimetering contour map

Elevation class	Range of Elevation m(ft)	Number of sampling sites	Percent of sampling sites
1	<304.8 (<1000)	0	
2	304.8-457.2 (1000-1500)	4	
3	457.2-609.6 (1500-2000)	4	67.4
4	609.6-762 (2000-2500)	9	
5	762-914.4 (2500-3000)	12	
6	914.4-1066.8 (3000-3500)	6	16.3
7	1066.8-1219.2 (3500-4000)	1	
8	1219.2-1371.6 (4000-4500)	3	14.0
9	1371.6-1524 (4500-5000)	3	
10	>1524 (>5000)	1	2.3

Table 1.2: Historical elevation bands for the 43 site survey

Table 1.1 represents the poorly distributed sites within elevation bands presented by Kenith Odom as table 38 in Odom (2003). His dissertation suggested a remodel of the survey from 90 sites to 43 and this table was used to suggest more high elevation sites. The survey was reduced from 90 sites down to 43 but the elevational distribution was not fixed. For comparison Table 1.2 shows the percentage of sites per elevation bands for the 43 site survey, just as Table 1.1 does for the 90 site survey. There are very few differences between the percentages, meaning there are still problems with the elevational distribution.

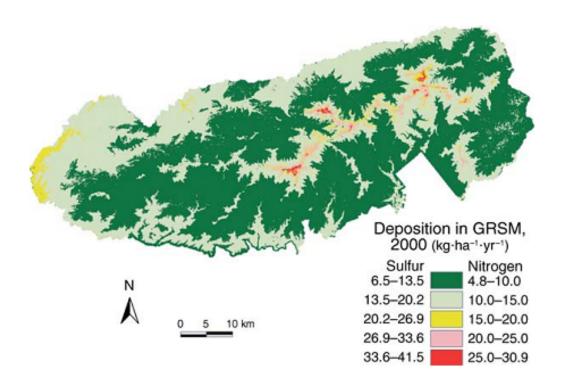


Figure 1.3: Modeled atmospheric deposition of N and S for the year 2000 and presented in Weathers et al. (2006).

For overall acidification of the GRSM, the high elevation bands could be the most important in the survey but they have the least amount of representation (John S. Schwartz, 2014). As can be seen in Figure 1.3, which is a model, the highest deposition of sulfur and nitrogen is at the highest elevations. This is because rainfall and fog in the GRSM affect elevations above 4000 feet first and higher elevations have steeper slopes, which correlate to both thinner soils and base poor geology. Sites in these areas continue to receive low pH values in samples and representation at these elevations is important. Unfortunately the tenth elevation class, according to Table 1.2, has only one site in it and one site cannot represent a whole elevation band.

Without adding sites, the easiest way to fix this poor distribution is to reorganize the elevation bands. For this paper the elevation bands were reassessed to strengthen the higher elevations.

**Table 1.3:** These elevation classes were created to add more weight to the higher elevations.

Elevation Classes	Meters (Feet)	n	Site #
1	304.8-609.6 (1000-2000)	5	13 ,23, 24, 30, 479
2	609.6-762 (2000-2500)	9	4, 311, 268, 480, 310, 483,
			147, 148, 484
3	$762-914.4 \ (2500-3000)$	13	114, 481, 482, 149, 66, 492,
			137, 293, 270, 493, 485, 144,
			224
4	914.4-1066.8 (3000-3500)	4	143, 142, 73, 71
5	1066.8-1371.6 (3500-4500)	4	74, 221, 251, 233
6	1371.6 < (4500 <)	2	253, 234

Table 1.3 contains all the sites used in the statistical analysis. Each of the statistical analyses in this paper will use these elevation bands to classify elevation for the stream survey data.

#### 1.4 Data Analysis Time Periods

Time trends are a general way to assess changing conditions of stream health in the GRSM. Instead of representing a single point in time like each grab sample, the trend analysis represents a site over time. The analysis can be used for the current quality of the streams in the survey along with trends to determine where the quality is headed. Trend analyses were conducted on the stream survey data in 2002 and published in Robinson et al. (2008) and then again in 2009 for the Biotics Effects report (John S. Schwartz, 2014). Though these papers analyzed similar years, Robinson et al. (2008):1993-2002 and John S. Schwartz (2014): 1993-2009, the results of these analyses are in disagreement. Of the ten elevation bands analyzed in Robinson et al. (2008) six had negative Julian date coefficients and the other four had no trend. The conclusion was reached that the pH is headed towards harmful and lethal conditions for aquatic life. In John S. Schwartz (2014), of the 67 sites studied in the biotic effects report most showed no trend, 22 showed an increase in pH and only 2 showed a decrease.

The opposite trends reported in Robinson et al. (2008) and John S. Schwartz (2014) suggest an inflection point in the trend line somewhere between 2002 and 2009. For this reason, and for easier comparison of results, a separate data set will be partitioned off from 1993 to 2002 to equal the years analyzed in Robinson et al. (2008). A third data set will be partitioned after the year 2008 because this is the year that the Kingston and Bull Run coal-fired power plants installed scrubbers onto their smoke stack exhaust. The hypothesis being the  $SO_4^{2-}$  concentrations will be noticeably different, and this difference could indicate greater  $SO_4^{-2}$  export from the soils. These three time sets will be analyzed separately (1993-2002, 2003-2008, 2009-2012).

#### 1.5 Data smoothing

It is rare for water quality data to be perfectly normal or parametric which is required for most statistical analysis. It is usually non-parametric and can contain recording errors and other influential values (Helsel and Hirsch, 1992). Four water quality variables will be used as dependents throughout this paper: pH, ANC, NO<sub>3</sub><sup>-</sup>,

 $SO_4^{2-}$ . Each of these dependents is important for studying acid deposition: pH and ANC directly relate the health of the streams,  $NO_3^-$  and  $SO_4^{2-}$  are the man-made pollutants thought to be causing increased acid deposition. Before these variables can be used as dependents they need to be analyzed for distribution, outliers, cycles, missing values, and serial correlation (Helsel and Hirsch, 1992). After initial analysis, all of the dependent vectors had outliers, most of these were found as a part of the step-wise regression process which highlights influential data for further analysis.

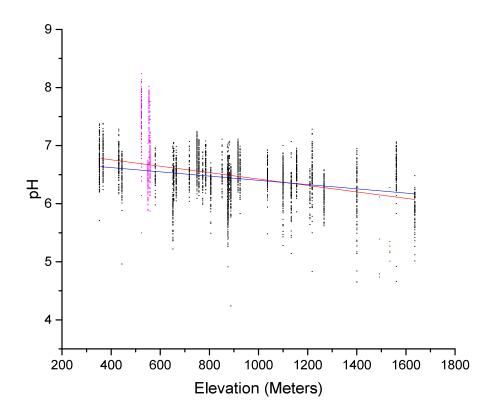


Figure 1.4: pH plotted vs. Elevation. With and without outliers.

The entire data smoothing process will not be shown here, but pH will be shown as an example. A figure of pH vs. month clearly shows seasonality, a pattern in pH based on the seasons, which is important to address for trend analysis (Helsel and Hirsch, 1992). Figure 1.4 shows the pH vs. elevation plot, which exhibits some

outliers but also a negative trend in pH as elevation increases. This graph includes two trend lines, one which represents the trend of all of the data points and the other representing a trend after the influential points are removed. Both trends are negative as elevation increases but the trend line containing the influential points is steeper.

Much of the variance in Figure 1.4 can be attributed to known influences in the stream survey data: Abram's creek watershed, sites that are affected by anakeesta geology, and storm flow (Neff et al., 2012). The anakeesta formation contains sulfidic slate, which can have the same negative effect of acid deposition, and keeps the pH values of streams very low. Site numbers 237 and 252 are sites that are downhill from road cuts that have exposed the underlying anakeesta formation to runoff, these sites have consistently low pH values compared to nearby sites. Comparatively, Abrams is a low elevation, low slope area where the underlying geology is Cades Sandstone, which buffers against acid rain extremely well. This sandstone contributes to high ANC values which in turn keep the mean pH levels higher than the rest of the sites in the survey.

Storm flow is both influential and detrimental to GRSM water quality. Storms can bring high intensity rainfall, quickly adding pollutants from rain, storm runoff, and pollutants left in the soil. Adding pollutants to streams with already low ANC and pH can be very harmful to aquatic life. Along with measured ANC, measurements taken from storm flow can show uncharacteristically low pH values and high amounts of metals from leaching. In this way, storm flow is sometimes considered an influential group on the rest of the data. Dr. Cai characterized all of the available water quality data between 1993 and 2010 as storm flow or base flow; this work is summarized in John S. Schwartz (2014). Because this classification ends at data collected in 2010, classifications for the years 2011 and 2012 would need to be tabulated for this paper. Quick analyses were run to see how influential storm flow was on the data as a whole, but results were inconclusive. Instead of dismissing all of the storm flow observations at once, single influential observations could be explained by storm flow

and removed. These observations can be removed on a case by case basis during the regression method in subsection 2.1.2.

#### 1.6 Objectives

Guidelines for this study were to:

- Characterize time trends in stream pH and acidic anions among elevation ranges in order to evaluate whether conditions are improving or degrading.
- Characterize sampling variance based on available water quality data, within the context of time and elevation, to support development of the GRSMs Vital Signs Monitoring Program.

The format of this thesis will follow these two objectives.

- Determine if stream pH and acid anion concentrations changed among three time periods (1993-2002, 2003-2008, and 2009-2012), and among six elevation ranges (1000-2000 ft, 2000-2500 ft, 2500-3000 ft, 3000-3500 ft, 3500-4500 ft, 4500< ft).</li>
  - Time trends (chapter 2)
  - Means Comparisons (chapter 3)
- Determine the statistical power for water quality parameters based on frequency and elevational location.
  - Post Hoc Analysis (chapter 4)
  - A Priori Analysis (chapter 4)

The thesis is organized into three separate chapters addressing the above research questions. Each chapter will follow the technical format of introduction, methods, results, and discussion.

# Chapter 2

# Trend Analysis

#### 2.1 Methods

#### 2.1.1 Introduction

Water quality data collected through the Park-wide Stream Survey can by analyzed with a trend analysis. It is used to determine the condition of the park's water bodies while trying to predict where the water quality is headed in the future. The sudden and gradual trends found through analysis are used in resource management by the National Park Service of the GRSM. A trend analysis on the stream survey data was conducted in 2002 and published in Robinson et al. (2008) and then again in 2009 for the Biotics Effects report (John S. Schwartz, 2014). Time trends for water quality variables in Robinson et al. (2008) were ascertained by regressing them by a Julian date time vector. Of the ten elevation bands analyzed in Robinson et al. (2008) six had negative Julian date coefficients and the other four had no trend. Of the 67 sites studied in the biotic effects report most showed no trend, 22 showed an increase in pH and 2 showed a decrease (John S. Schwartz, 2014). The trend analysis of Robinson et al. (2008) used data from the 90 site survey while the trend analysis in John S. Schwartz (2014) used only 67. The difference in survey sites may affect the trend analysis, and for this reason both time periods will be analyzed separately

to test this hypothesis. The trend analysis will use stream survey data from 1993 to 2012 using the statistical programs JMP and SPSS for analysis.

#### 2.1.2 Step-wise regression

A general method of trend analysis is linear regression with time as a factor.

$$Y = \beta_0 + \beta_1 T + \beta_2 X + \epsilon \tag{2.1}$$

Regression requires the data to be parametric (normal distribution) and for the data to be adjusted for X, which means that inherent variation should be removed Much of the explained variation was handled in before regression takes place. section 1.5 but some variation comes from single observations which are termed influential observations. Removal of excess variation is a standard process in stepwise regression modeling. Influential observations are identified through several tests available through SPSS. The different tests applied for this paper include tests for normality, heteroscedasticity, cook's D, DFBETAS, and DFFITS. As observations were identified by cook's d, DFBETAS, and or DFFITS as influential, they were individually analyzed to determine influential factors. Modification or removal of an influential observation had to be justified, or it would remain an outlier. For example, a pH value that read as 16.47 was changed to 6.47. In addition, some conductivity values were obvious copies of the ANC value for the same observation and were removed. Some influential observations were not as obvious; if they could not be labeled as storm flow or human error they would be kept. After sufficient attention was given to the influential observations, step-wise regression was re-run and more influential observations were found, and attention would need be given to those as well.

The step-wise selection process adds and removes predictors based on limits imposed by the user. In this case the F test statistic was utilized which is used as a test of fit within the data. A variable with a F test statistic of .05 or higher can

enter but would be removed if it exceeded .10. The variables available for selection were chosen from those water quality parameters monitored by the Stream Survey. One benefit of choosing only variables directly from the stream survey dataset is a high ease of repeatability for the future. The models created to explain pH, ANC,  $NO_3^-$ , and  $SO_4^{2-}$  are presented in Table 2.1. If any of the time variables were chosen by the step-wise method, the others were forced in. This was done to ensure the Julian date coefficient was present along with  $\sin(\theta)$  and  $\cos(\theta)$  for seasonality. Many variables are present in the stream survey database, some are measurements but others were derived. Mathematically, seasonality can be modeled with the  $\sin(\theta)$  and  $\cos(\theta)$  variables as shown in Helsel and Hirsch (1992). They represent each day of the year as a fraction of the year and place the lowest pH on January 1 and the highest on July 1. The variable BC (base cations) represent the sums of the  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ , and  $Na^+$  concentrations. Correlations were run between each of the proposed variables and both ANC and BC were found to be better described as  $\log_2(ANC)$  and  $\log_2(BC)$  when explaining pH.

**Table 2.1:** Equations created through step-wise variable selection

Dependent (n)	Model	Adjusted $r^2$	Model p
pH (3116)	$.673 \times \log_2(\text{Sum Base Cations}) + (368 \times$	0.630	< 0.001
	$NO_3$ ) + (.262 × Julian Day) + (266 × $SO_4$ ) + (050 × $cos(\theta)$ )		
ANC $(3116)$	(.415 $\times$ Sum Base Cations) + (185 $\times$	0.984	0.049
	$SO_4$ ) + $(.595 \times Conductivity)$ + $(102 \times Conductivity)$		
	$NO_3$ + $(.019 \times Julian Date) + (.005 \times Cl) + (.005 \times Cl)$		
NO (2442)	$(.005 \times \sin(\theta))$	0.400	0.04
$NO_3$ (3116)	$(295 \times SO_4) + (-3.183 \times ANC) +$	0.498	0.017
	$(2.19 \times \text{Conductivity}) + (.923 \times)$		
	Sum Base Cations) + $(.120 \times 1.120 \times $		
	Julian Date) + $(.051 \times Cl)$ + $(.047 \times cir(0))$		
CO (2116)	$\sin(\theta)$ ) + $(.031 \times \cos(\theta))$	0.720	<0.001
$SO_4$ (3116)	$(166 \times NO_3) + (2.318 \times Conductivity) +$	0.720	< 0.001
	$(-3.229 \times ANC) + (1.033 \times Sum Page Cations) + (0.042 \times Inlian Page)$		
	Sum Base Cations) $+$ (.042 $\times$ Julian Date)		

The difficulty in modeling a time trend comes from the high amount of variation within the datasets. This variation is explained by X in Equation 2.1 and sometimes it is unclear if the trend in Y (dependent) is due to T (time) or X (independent). All of the equations contain the time variables (Julian date,  $\sin(\theta)$ , and  $\cos(\theta)$ ) along with the chosen chemical variables. Because of the difficulty of explaining what the Julian date coefficient really means alongside the chemical variables a second set of equations was created for analysis. Theses equations use only the three time variables to describe each of the dependents, only T variables, no X variables. Table 2.2 can be used as a summary of the step-wise process.

**Table 2.2:** List of variables used for step-wise variable selection. X's for variables selected by the step-wise method, O's if variable was added after the step-wise process.

		Depen	dents for	step-wise	e regression
Available Variables	comments	рН	ANC	$NO_3$	$SO_4$
рН	Dependent				
ANC	Dependent			X	X
$NO_3$	Dependent	X	X		X
$SO_4$	Dependent	X	X	X	
Julian Date	Time		X	X	X
Month	Time				
Year	Time				
Julian Date Days	Seasonality	X			
$\sin(\theta)$	Seasonality	Ο	X	X	O
$\cos(\theta)$	Seasonality	X	O	X	O
Sum Base Cations	$Ca^{2+}, Mg^{2+}, K^+, Na^+$		X	X	X
Conductivity			X	X	X
Chloride			X	X	
Elevation	Meters				
Slope					
$\log_2 (ANC)$	Transformation				
$\log_2$ (Base Cations)	Transformation	X			
Number of predictors		6	8	8	7

#### 2.2 Results

Trends in Robinson et al. (2008) are reported by the Julian date time coefficient for the dependent variables (pH, ANC,  $NO_3^-$ ,  $SO_4^{2-}$ ) for each of the eleven historical elevation bands. The Julian date coefficient was used in this paper to reflect a time trend as well. 144 different Julian date coefficients were calculated and are presented in two tables. Equations calculated using the step-wise equations are presented in subsection 2.2.1 and the equations calculated using the three time variables only are recorded in subsection 2.2.2. Each trend line is represented by its Julian date coefficient, the  $r^2$  value for the trend line, and its statistical significance.

Only 2 of the 72 trend lines calculated from the step-wise equations (subsection 2.2.1) are insignificant, while 50 of the 72 trend lines calculated using the time variable equations (subsection 2.2.2) are insignificant. Insignificance is caused by a regression line with a p-value greater than the chosen  $\alpha$  of .05. When this happens the hypothesis that  $\beta \neq 0$  is rejected. Meaning that there is greater than a 5% chance that  $\beta = 0$  which in this case means that the Julian date coefficient = 0 and there is no time trend.

#### 2.2.1 Step-wise Julian date coefficients

pH pH time trends were negative for only three statistically significant regression lines, all in time set 1 (Table 2.3), in elevation classes 2 (-0.091), 3 (-0.010), and 5 (-0.157). There is one insignificant negative trend in time set 3 (Table 2.5) in the fifth elevation class. Overall pH in the park is increasing over time.

**ANC** While evaluating across time sets and elevation classes, trends for ANC fluctuate. In fact eleven of the lines are positive, and seven are negative. Two of the three negative trends for ANC in time set 2 (Table 2.4) have a smaller slope in time set 3 (Table 2.5): class 1 (-0.004  $\mu eqL^{-1}$ ) and class 4 (-0.028  $\mu eqL^{-1}$ ) decrease to -0.002  $\mu eqL^{-1}$  and -0.006  $\mu eqL^{-1}$  respectively. One of the negative trends in time

**Table 2.3:** Julian date coefficients from step-wise regression for set 1.

Elevation class	Elevation range m (ft)	Number of sites	Julian date coefficient, $\mu$ eq/L or pH units (model adjusted $r^2$ ) (p-value)			
CIABS	range in (10)	51005	pН	ANC	Nitrate	Sulfate
	304.8-609.6		0.069	0.007	0.034	-0.096
1	(1000-2000)	5	0.712	0.985	0.503	0.569
	(1000 2000)		0.000	0.000	0.000	0.000
	609.6-762		-0.091	-0.036	-0.037	0.019
2	(2000-2500)	9	0.388	0.603	0.699	0.766
	(2000-2500)		0.000	0.000	0.000	0.000
	762-914.4 (2500-3000)	13	-0.010	0.008	-0.013	0.024
3			0.693	0.971	0.359	0.590
			0.000	0.000	0.000	0.000
	014410000	4	0.019	0.015	0.058	0.061
4	914.4-1066.8 (3500-3500)		0.205	0.709	0.410	0.402
	(3300-3300)		0.000	0.000	0.000	0.000
	1066.8-1371.6	4	-0.157	-0.082	0.288	-0.133
5	(3500-4500)		0.165	0.760	0.328	0.566
	(3000-4000)		0.010	0.000	0.000	0.000
	1371.6<	2	0.218	0.067	-0.011	0.092
6			0.505	0.802	0.871	0.716
	(4500 <)		0.000	0.000	0.000	0.000

**Table 2.4:** Julian date coefficients from step-wise regression for set 2.

Elevation class	Elevation range m (ft)	Number of sites	Julian date coefficient, $\mu$ eq/L or pH units (model adjusted $r^2$ ) (p-value)			
Class	range in (10)	51005	рН	ANC	Nitrate	Sulfate
	304.8-609.6		0.150	-0.004	0.038	0.039
1	(1000-2000)	5	0.781	0.996	0.551	0.673
	(1000 2000)		0.000	0.000	0.000	0.000
	609.6-762		0.275	0.033	0.044	0.044
2	(2000-2500)	9	0.348	0.779	0.816	0.893
	(2000-2000)		0.000	0.000	0.000	0.000
	762-914.4 (2500-3000)		0.156	0.005	0.072	0.034
3		13	0.663	0.996	0.637	0.923
			0.000	0.000	0.000	0.000
	014410660	4	0.249	-0.028	0.092	0.110
4	914.4-1066.8 (3500-3500)		0.400	0.779	0.405	0.343
	(3300-3300)		0.000	0.000	0.000	0.000
	1066.8-1371.6		0.137	-0.020	0.204	0.135
5	(3500-4500)	4	0.300	0.739	0.562	0.884
	(5500-4500)		0.027	0.000	0.001	0.000
	1371.6<		0.359	0.127	0.074	0.161
6		2	0.317	0.812	0.832	0.844
	(4500 <)		0.000	0.000	0.000	0.000

**Table 2.5:** Julian date coefficients from step-wise regression for set 3.

Elevation class		Number of sites	Julian date coefficient, $\mu$ eq/L or pH units (model adjusted $r^2$ ) (p-value)			
CIASS	range in (10)	51005	рН	ANC	Nitrate	Sulfate
1	304.8-609.6	5	0.106 0.894	-0.002 0.989	0.026 0.376	-0.052 0.536
	(1000-2000)		0.000 0.000	0.000	0.000	
	609.6-762		0.218	0.069	0.121	0.039
2	(2000-2500)	9	0.606	0.862	0.735	0.887
	(2000 2000)		0.000	0.000	0.000	0.000
	762-914.4	13	0.056	0.007	0.019	0.050
3	(2500-3000)		0.766	0.997	0.598	0.915
			0.000	0.000	0.000	0.000
	914.4-1066.8	4	0.413	-0.006	-0.013	-0.068
4	(3500-3500)		0.593	0.772	0.635	0.529
	(5500 5500)		0.000	0.000	0.000	0.000
	1066.8-1371.6	4	-0.115	0.901	0.098	0.015
5	(3500-4500)		0.158	0.540	-0.272	0.658
	(3300-4300)		0.130	0.001	0.975	0.000
	1371.6<	2	0.289	0.059	0.097	-0.059
6	(4500 <)		0.286	0.809	0.881	0.861
	(4000 < <i>)</i>		0.000	0.000	0.000	0.000

set 2 (Table 2.4) becomes positive in time set 3 (Table 2.5), class 5 (-0.020  $\mu eqL^{-1}$ ) increased to 0.901  $\mu eqL^{-1}$ . When comparing concentrations in time set 2 (Table 2.4) to time set 3 (Table 2.5), ANC trends on average are growing over time.

Nitrate The trends for NO<sub>3</sub><sup>-</sup> in time set 1 (Table 2.3) are half positive and half negative. The trends in time set 2 (Table 2.4) are all positive, but there is a decreasing trend in time set 3 (Table 2.5), elevation class 4 of -0.006  $\mu eqL^{-1}$ .

Sulfate  $SO_4^{2-}$  contains mixed positive and negative trends for time set 1 (Table 2.3) but all positive trends for time set 2 (Table 2.4). Half of the  $SO_4^{2-}$  trends in time set 3 (Table 2.5) are negative in elevation bands 1 (-0.052  $\mu eqL^{-1}$ ), 3 (-0.068  $\mu eqL^{-1}$ ), and 6 (-0.059  $\mu eqL^{-1}$ ).

#### 2.2.2 Julian date coefficients from time variables only

Only 20 of these 72 regression lines are significant, which are those that have acceptable p-values less than .05.

**pH** The dependent variable pH in time set 1 (Table 2.6) has zero significant lines, time set 2 (Table 2.7) and time set 3 (Table 2.8) combined contain slightly less than half insignificant trend lines. The insignificance of the trend lines leaves them untrustworthy, but the trend values themselves are similar to those calculated from the step-wise equations (subsection 2.2.1).

**ANC** There are only two significant regression lines for ANC. Elevation class 5 in time set 1 (Table 2.6) has a decreasing trend of -.148  $\mu eqL^{-1}$ , and while there are no significant lines in time set 2 (Table 2.7), time set 3 (Table 2.8) elevation class 5 has a single positive trend of .891  $\mu eqL^{-1}$ .

Nitrate and Sulfate NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> both had negative trends in time set 1 (Table 2.6) class 1, -0.138  $\mu eqL^{-1}$  and -0.190  $\mu eqL^{-1}$ . These are the only significant

**Table 2.6:** Julian date coefficients from the time variable equations for set 1.

Elevation class	Elevation range m (ft)	Number of sites	Julian date coefficient, $\mu$ eq/L or pH units (model adjusted $r^2$ ) (p-value)			-
CIASS	range in (10)	51005	рН	ANC	Nitrate	Sulfate
1	304.8-609.6 (1000-2000)	5	$0.054 \\ 0.047$	$0.089 \\ 0.024$	-0.138 0.016	-0.190 0.045
	(1000 2000)		0.321	0.106	0.022	p-value)  Sulfate  -0.190 0.045 0.001  -0.075 0.009 0.142 -0.047 -0.004 0.355  0.095 -0.016 0.313  0.092 -0.010 0.331 -0.036 -0.009
2	609.6-762 (2000-2500)	9	-0.090 0.128 0.060	-0.060 $0.189$ $0.195$	-0.060 $0.017$ $0.248$	0.009
3	762-914.4 (2500-3000)	13	-0.012 0.013 0.817	-0.030 0.000 0.550	-0.048 -0.004 0.365	-0.047 -0.004
4	914.4-1066.8 (3500-3500)	4	-0.047 0.059 0.597	-0.151 0.294 0.055	-0.009 -0.027 0.926	-0.016
5	1066.8-1371.6 (3500-4500)	4	-0.151 0.051 0.100	-0.148 0.381 0.047	0.330 0.120 0.006	-0.010
6	1371.6< (4500 <)	2	$\begin{array}{c} 0.156 \\ 0.096 \\ 0.092 \end{array}$	-0.016 0.075 0.863	-0.208 $0.092$ $0.058$	

**Table 2.7:** Julian date coefficients from the time variable equations for set 2.

Elevation class	Elevation range m (ft)	Number of sites	Julian date coefficient, $\mu$ eq/L or pH units (model adjusted $r^2$ ) (p-value)			
CIASS	range in (10)	51005	рН	ANC	Nitrate	Sulfate
	304.8-609.6		0.139	0.009	0.155	0.192
1	(1000-2000)	5	0.040	0.001	0.061	0.043
	(1000-2000)		0.025	0.888	0.012	0.002
	609.6-762		0.145	-0.090	0.178	0.138
2	(2000-2500)	9	0.061	0.081	0.043	0.014
	(2000-2000)		0.012	0.114	0.002	0.017
	762-914.4	13	0.103	-0.006	0.047	0.099
3	(2500-3000)		0.020	-0.003	-0.003	0.006
	(2000-0000)		0.075	0.925	0.418	0.085
	914.4-1066.8		0.235	-0.029	0.193	0.192
4	(3500-3500)	4	0.148	0.180	0.086	0.023
	(3300-3300)		0.007	0.728	0.030	0.035
	1066.8-1371.6	4	0.135	-0.112	-0.176	0.067
5	(3500-4500)		-0.069	0.337	-0.082	-0.024
	(5500-4500)		0.466	0.443	0.401	0.701
	1371.6<		0.204	-0.108	0.236	0.307
6	(4500 <)	2	0.081	0.094	0.046	0.074
	(4000 < )	`-)	0.041	0.274	0.020	0.002

**Table 2.8:** Julian date coefficients from the time variable equations for set 3.

Elevation class	Elevation range m (ft)	Number of sites	Julian date coefficient, $\mu$ eq/L or pH units (model adjusted $r^2$ ) (p-value)			
Class	range in (10)	51005	рН	ANC	Nitrate	Sulfate
1	304.8-609.6 (1000-2000)	5	$0.111 \\ 0.028$	$0.026 \\ 0.000$	-0.036 0.018	-0.092 0.005
	( )		0.122	0.718	0.619	0.207
2	609.6-762	9	$0.141 \\ 0.052$	$0.017 \\ 0.056$	$0.020 \\ 0.011$	-0.062 -0.010
	(2000-2500)	Ü	0.037	0.800	0.767	0.376
3	762-914.4 (2500-3000)	13	-0.034 -0.009	-0.027 -0.002	-0.036 -0.004	0.078 -0.007
	(2500-5000)		0.611	0.684	0.592	0.246
4	914.4-1066.8	4	0.405 0.200	$0.032 \\ 0.161$	-0.067 -0.016	-0.129 -0.011
	(3500-3500)		0.000	0.733	0.518	0.215
5	1066.8-1371.6	4	-0.031 0.218	0.891 0.466	0.052 -0.039	-0.414 -0.076
	(3500-4500)		0.934	0.007	0.904	0.347
	1371.6<		0.264	0.083	-0.021	-0.214
6	(4500 <)	2	0.039	0.058	-0.016	0.007
	(4500 <)		0.023	0.462	0.859	0.068

decreasing trends exhibited for either  $NO_3^-$  or  $SO_4^{2-}$  from trends calculated with the time variable equations (subsection 2.2.2). Both have positive trends in time set 2 (Table 2.7) at elevation classes 1, 2, 4 and 6. Neither water quality variables have a significant trend in time set 3 (Table 2.8).

## 2.2.3 Elevation trends

**Table 2.9:** Dependents regressed against elevation (m) only.

set	Dependent	n	slope	$r^2$	per +1000m
1	рН	1357	.000	.173	-0.411
	ANC	1354	056	.199	-56.227
	$NO_3^-$	1161	.032	.372	32.211
	$SO_4^{2-}$	1343	.037	.108	37.371
	SBC	1358	.013	.005	13.065
2	рН	997	.000	.094	-0.391
	ANC	997	051	.157	-50.970
	$NO_3^-$	995	.031	.307	30.677
	$SO_4^{2-}$	1029	.036	.098	35.793
	SBC	1031	.016	.009	15.537
3	рН	757	.000	.061	-0.286
	ANC	757	036	.087	-35.689
	$NO_3^-$	757	.026	.195	25.924
	$SO_4^{2-}$	757	.030	.101	29.715
	SBC	757	.020	.014	19.905

The aim of Table 2.9 is to calculate the change in water quality values for every 1000 meters of elevation. The base cations were added as a dependent for this analysis. All of the pH and ANC values decrease as elevation increases and all of the  $NO_3^-$ ,  $SO_4^{2-}$ , and base cations dependents increase as elevation increases. Except for the base cations all of the elevational trends for the water quality dependents decrease over time.

### 2.2.4 Results by Comparison

In comparing Table 4 from Robinson et al. (2008) with time set 1 (Table 2.3) from this study, it needs to be noted that along with the elevation classes being different, the stream survey data has changed over the years. The largest difference in the data analyzed in Robinson et al. (2008) and this paper is the reduction from 90 sites to 43 sites. Another difference is that the Abrams creek sites were not included in this study, but they were included in Robinson et al. (2008). These changes could explain the difference in pH trends seen in the old elevation classes from Robinson et al. (2008) of 1 (-0.0127), 2 (-0.0186), and 3 (-0.0260) compared to elevation class 1 (0.069) in this study. Two sites (237, 252) that would be in the new elevation class 6 were left out of this statistical analysis as influential observations, which correspond to the historical elevation class 9 in the other analysis.

One interesting comparison between Table 4 of Robinson et al. (2008) and time set 1 (Table 2.3) of this study are the differences in pH coefficients. All of the pH trends presented in Table 4 of Robinson et al. (2008) are negative which led to the statements that pH is dropping and can continue to dangerous levels in the future. However, only half the time trend trends in time time set 1 (Table 2.3) of pH found in this study were negative. All the rest of the pH trends for Julian date for both of the current trend analyses are positive when they are significant.

pH and ANC For a stream survey data set of 92 sites within the time frame of 1993 to 2009 John S. Schwartz (2014) reports a decrease for pH and ANC of -0.32 pH units and -35.73  $\mu$ eq L<sup>-1</sup> per 1000-ft elevation gain or 302-m elevation gain respectively. Multiplying these results by 3.3 to convert to meters and pH and ANC are -1.056 pH units and -117.909  $\mu$ eq L<sup>-1</sup> per 1000-m elevation gain respectively. By comparing the metric results from John S. Schwartz (2014) to those from Table 2.9 it can be seen that in time set 3, both pH and ANC are significantly lower with trends of -.0286 pH units and -35.689  $\mu$ eq L<sup>-1</sup> per 1000-m increase respectively. The results could be affected by the differing amounts of time and number of sites in each study.

Nitrate and Sulfate The positive  $SO_4^{2-}$  trends seem to decrease by 2  $\mu$ eq L<sup>-1</sup> between set 1 and set 2 in Table 2.9 and then by 6  $\mu$ eq L<sup>-1</sup> between set 2 and 3. In contrast, a negative insignificant elevational trend was found in John S. Schwartz (2014) for the years 1993 to 2009.

 $NO_3^-$  follows a similar pattern as  $SO_4^{2-}$ , increasing as elevation increases but decreasing over time, which is also in agreement with findings in Weathers et al. (2006). As the trends for  $NO_3^-$  and  $SO_4^{2-}$  decrease over the time sets the base cations increase by 2  $\mu$ eq L<sup>-1</sup> between set 1 and set 2 and then by almost 5  $\mu$ eq L<sup>-1</sup> between set 2 and set 3.

## 2.3 Discussion and Conclusions

It is interesting that the step-wise process did not choose elevation as an explanatory independent variable (X) for any of the dependents (Y), because many studies have declared elevation a significant explanation of variation and Figure 1.4 clearly shows a decreasing trend for pH while increasing the elevation. Increasing acidification with increased elevation was observed in John S. Schwartz (2014) for data collected between 1993 and 2009. This suggests that there is an elevation trend; it is just not as important as other factors when studying acidification in the GRSM. In fact, the elevation classes themselves characterize elevation and the individual elevation classes might be too small to show a significant elevation trend.

At this time, the data shows that water quality is increasing. However, the relatively insignificant trends from the time variable equations (subsection 2.2.2) suggest that the increase in pH over time is due to other factors, which were included with the step-wise selection. In light of other studies such as Robinson et al. (2008), the results of this paper agree with John S. Schwartz (2014) that pH is increasing over time.

 $SO_4^{2-}$  has more decreasing trends over time for the years 2009 to 2012 than in any other time set. This is not surprising based on the values shown in Figure 3.1

in which  $SO_4^{2-}$  concentrations at the Noland Divide high elevation site begin to drop along with emissions from Kingston and Bull run power plants.

Water quality is increasing. pH and ANC values are rising and the acid anions,  $NO_3^-$  and  $SO_4^{2-}$ , are decreasing. The concerns of lowering pH raised in Robinson et al. (2008) are now not as important as those for  $SO_4^{2-}$  desorption raised in John S. Schwartz (2014). The lack of elevation trend in  $SO_4^{2-}$  was attributed to high elevation soil adsorption of depositional  $SO_4^{2-}$  and a statement was made that  $SO_4^{2-}$  remains absorbed to soil particles as long as soil water chemistry remains high in  $SO_4^{2-}$  concentration and low in pH (Cai et al., 2011). The slope for the elevation trend of  $SO_4^{2-}$  over the three sets is decreasing but most of the mean  $SO_4^{2-}$  concentrations listed in Appendix B (descriptive statistics) are increasing through time along with pH. This suggests desorption of  $SO_4^{2-}$  into the streams, thus raising the lower elevation  $SO_4^{2-}$  concentrations up to the higher concentrations of upper elevation sites.

## Chapter 3

# **ANOVA** Means Comparison

## 3.1 Methods

#### 3.1.1 Introduction

Both the Bull Run and Kingston power plants installed scrubbers on their smokestacks in the year 2008 in order to reduce sulfate and nitrate emissions. These scrubbers have significantly reduced the amount of sulfur dioxide emitted by the smoke stacks. According to Figure 3.1, which is a bar chart depicting the sum of sulfur dioxide emissions of Kingston and Bull Run power plants, the sulfur dioxide concentration dropped from 80 thousand tons in 2008 to about 15 thousand tons in 2009.

Noland divide is a high elevation site located just below Clingman's Dome, which is the highest point in the Great Smokey Mountains. It has been studied for acid deposition since the late 80's and contains three separate sample collection sites. The through fall site collects deposition that has had a chance to fall through the trees and thus collects extra pollutants resting there. There is also an open to air site, which is designed to collect deposition that has not run through the trees and then grab samples are collected from two nearby streams. Samples from Noland Divide

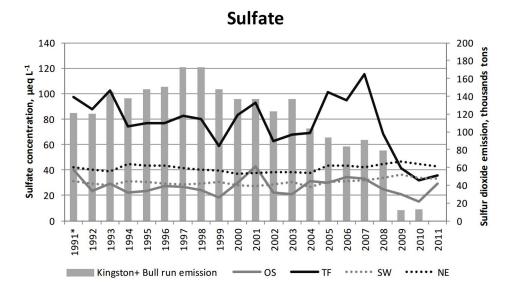


Figure 3.1: Yearly sulfur dioxide emissions for Kingston and Bull Run, with yearly Noland Divide high elevation site sulfate concentrations. Figure borrowed from John S. Schwartz (2014).

are continuously collected and analyzed every two weeks with the same lab processes as the Park-wide Stream Survey samples.

Interestingly the through fall  $SO_4^{2-}$  concentrations dramatically decline from about 115  $\mu$ eq  $L^{-1}$  in 2007 to about 30  $\mu$ eq  $L^{-1}$  in 2010. A reduction in sulfur dioxide emissions could correlate to a reduction in  $SO_4^{2-}$  concentrations measured from the Noland Divide through fall. The effects of air pollution will be more pronounced and easier to recognize at a high elevation site such as Noland Divide but one site cannot represent the whole park. The geographical spread and number of sites contained within the Park-wide Stream Survey can give a fuller representation of the effects of air pollution from local power plants. Assuming that the sulfur dioxide emissions

from Kingston and Bull Run power plants affect the whole GRSM park, there may be signals for this effect in the data. To explore for these signals each water quality variable in each time set will be tested against each other by way of means comparison methods. A significant difference between the data before and after the scrubbers were installed would indicate reason for further study.

#### Instruments

ANOVA is a common means comparison method, but it is not best when testing multiple hypotheses at one time. As more hypotheses are added the chances of finding a rare occurrence rises, which is the chance to reject the null hypothesis (the means being equal) when it is actually true (type I error). The proposed study requires testing for the equality of three separate time sets and thus three separate hypotheses at once. The Bonferroni adjustment solves this by dividing the alpha by the number of hypotheses being tested. Technically SPSS multiplies the p-value of the least significant differences (LSD) by the number of tests (IBM, 2013). In this way multiple hypothesis are tested as if there is only one.

Two outputs are created by the Bonferroni method: one graphical and one numerical. The graphical output presents a line graph showing the means of each group analyzed. An observer can use this output to see the actual group means along with a visual representation of their differences. The numerical output presents a table of pairwise listings of all the groups compared to each other. Each pair listed is evaluated by their 95% confidence intervals and the significance associated with each comparison. If the confidence interval includes zero then the groups are statistically the same or equal.

Using SPSS and the Bonferroni method three time sets (93-02, 03-08, 09-12) will be compared at six elevation class levels and across four water quality variables (pH, ANC,  $NO_3^-$ , and  $SO_4^{2-}$ ). Each group compared are the same data groups from the park-wide stream survey data analyzed for trend analysis (chapter 2) and power analysis (chapter 4).

## 3.2 Results

Table 3.1: Bonferroni comparisons between multiple groups

Elevation Classes		рН			ANC		ľ	Vitrat	e	Ç	Sulfat	e
	1-2	1-3	2-3	1-2	1-3	2-3	1-2	1-3	2-3	1-2	1-3	2-3
1	$\neq$	$\neq$	$\neq$	=	=	=	$\neq$	=	=	=	=	=
2	=	=	=	=	$\neq$	=	$\neq$	$\neq$	=	$\neq$	$\neq$	=
3	$\neq$	$\neq$	$\neq$	=	$\neq$	=	=	$\neq$	$\neq$	=	=	=
4	=	$\neq$	$\neq$	=	=	=	=	=	=	=	=	=
5	$\neq$	$\neq$	$\neq$	=	$\neq$	$\neq$	$\neq$	=	$\neq$	=	=	=
6	=	$\neq$	$\neq$	=	=	=	=	=	=	=	=	=

The group means comparisons are represented by equal signs and unequal signs and are taken from the 95% C.I. determined by SPSS. In Table 3.1 there are three columns per water quality variable and each column represents the comparison of two groups of the same variable in different times. All groups that were found to be equal were insignificant, and all groups that were unequal are significant at the family wise  $0.05~\alpha$  level.

The line graphs can be helpful in comparing the sizes of mean differences between the three time sets. These figures are not as definitive as the results in Table 3.1 because a noticeable visual difference does not always correspond to a significant difference, but they can still be useful as visual tools. There are six figures for each of the water quality variables, one for each of the elevation classes.

Figure 3.2: pH set means, class 1

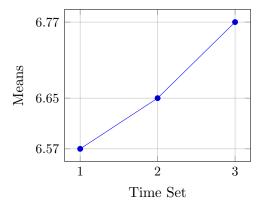


Figure 3.4: pH set means, class 3

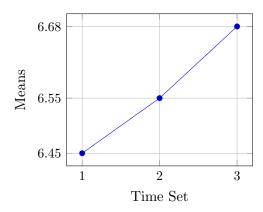


Figure 3.6: pH set means, class 5

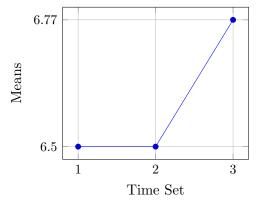


Figure 3.3: pH set means, class 2

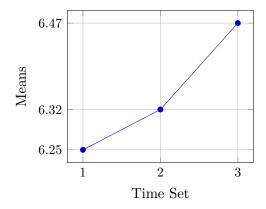


Figure 3.5: pH set means, class 4

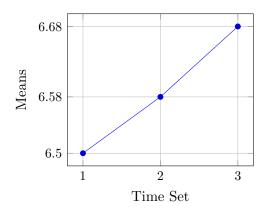


Figure 3.7: pH set means, class 6

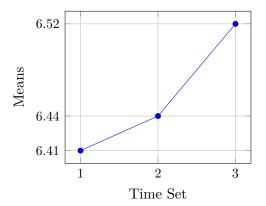


Figure 3.8: ANC set means, class 1

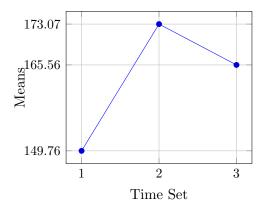


Figure 3.10: ANC set means, class 3

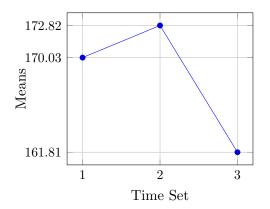


Figure 3.12: ANC set means, class 5

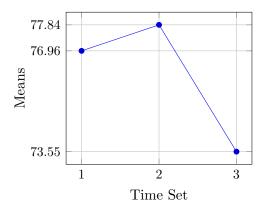


Figure 3.9: ANC set means, class 2

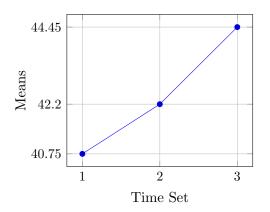


Figure 3.11: ANC set means, class 4

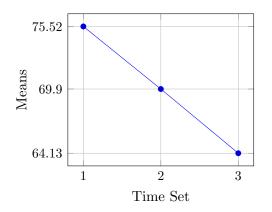


Figure 3.13: ANC set means, class 6

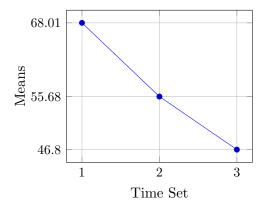
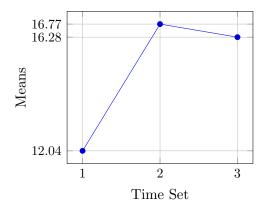
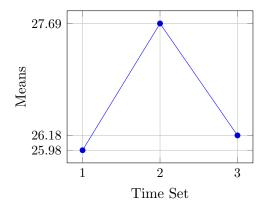


Figure 3.14:  $NO_3^-$  set means, class 1



**Figure 3.16:**  $NO_3^-$  set means, class 3



**Figure 3.18:**  $NO_3^-$  set means, class 5

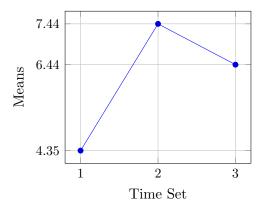
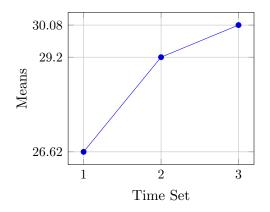


Figure 3.15:  $NO_3^-$  set means, class 2



**Figure 3.17:**  $NO_3^-$  set means, class 4

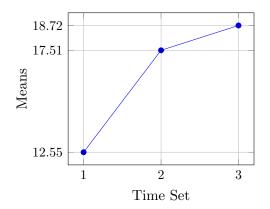


Figure 3.19:  $NO_3^-$  set means, class 6

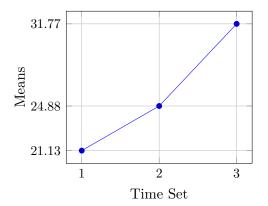


Figure 3.20:  $SO_4^{2-}$  set means, class 1

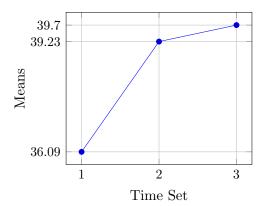


Figure 3.22:  $SO_4^{2-}$  set means, class 3

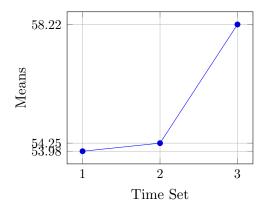


Figure 3.24:  $SO_4^{2-}$  set means, class 5

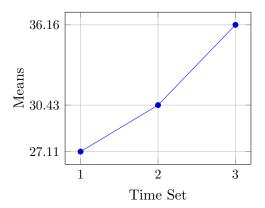


Figure 3.21:  $SO_4^{2-}$  set means, class 2

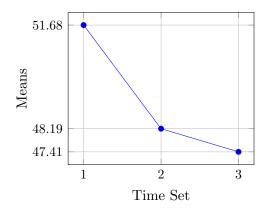


Figure 3.23:  $SO_4^{2-}$  set means, class 4

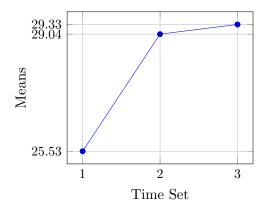
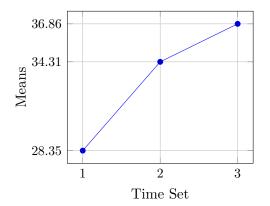


Figure 3.25:  $SO_4^{2-}$  set means, class 6



pH The time set comparisons for pH are the first presented, they include 13 unequal comparisons out of 18, more inequalities than any other water quality variable. Elevation class 2 contains all three equal comparisons and class 4 and 6 are equal across sets 1 and 2. If a pronounced elevational trend existed for pH in the GRSM, this trend would be visible in the Bonferroni line graphs. Following the means of each time set through the different elevation classes the largest mean should be in elevation class 1 (Figure 3.2) and the smallest in elevation class 6 (Figure 3.7). Unfortunately elevation class 2 (Figure 3.3) always contains the lowest means instead of elevation class 6 (Figure 3.7). And elevation class 3 (Figure 3.4) behaves as if it should be between elevation class 5 (Figure 3.6) and 6 (Figure 3.7).

ANC In contrast to the pH line graphs, the ANC line graphs do not all have similar rates of change. In the odd numbered elevation classes ANC reached a peak in time set 2 and decreased for time set 3. All of the ANC figures have a decreasing trend from time set 2 to 3 except for elevation class 2 which is steadily increasing. The time set means presented in the ANC figures vary greatly in concentration. Elevation classes and 1 (Figure 3.8) and 2 (Figure 3.9) are more than double the means of the other classes. The ANC concentrations of elevation class 2 (Figure 3.9) are the lowest which helps explain why the pH of elevation class 2 (Figure 3.3) is also the lowest. It is important to note here that even though elevation class 2's concentrations are the lowest, they are also the only concentrations that are increasing over time. The study found more equality than inequality while comparing time sets, and in fact all three time sets in elevation classes 1, 4, and 6 were found to be equal. Only 4 time set comparisons were found to be unequal: comparisons between time sets 1 and 3 at elevation classes 2, 3, and 5, and the comparison between time sets 2 and 3 at elevation class 5.

Nitrate  $NO_3^-$  elevation classes 4 and 6 are statistically equal across all time sets and elevation class 3 shows time sets 1 and 2 being equal while 3 is not. Elevation

class 1 is the opposite of expected (all time sets are unequal with time set 3) showing all being equal except for sets 1 and 2. In elevation class 2 time sets 2 and 3 are equal and in elevation class 5 time sets 1 and 3 are equal. The line graphs for the odd numbered elevation classes of  $NO_3^-$  all have decreased mean values from sets 2 to 3. In elevation classes 2 (Figure 3.15) and 4 (Figure 3.17) the mean values for time set 3 are higher than those in time set 2 but the difference of the means over time is decreasing. Overall the  $NO_3^-$  figures show mostly decreasing concentrations over time, except for elevation class 6 (Figure 3.19) which is always increasing. The odd classes all have decreasing negative trends from time sets 2 to 3 while elevation classes 2 and 4 have decreasing positive trends between sets 2 and 3.

Sulfate The time set comparisons of  $SO_4^{2-}$  point to all three time sets being equal across all elevation classes except for class 2 (Figure 3.21), which shows equality between time sets 2 and 3. The line graphs can sometimes be misleading when visually comparing the time set means, and it is always best to have the confidence intervals on hand. For example when looking at the  $SO_4^{2-}$  figures many of the means look different across the time sets, but according to the table, except for class 2, they are all equal across time sets. All of the set 3 means for  $SO_4^{2-}$  are larger than their respective set 2 means except for those in elevation class 2 (Figure 3.21) which has negative trends throughout.

## 3.3 Discussion and Conclusions

This analysis was completed in expectation of patterns similar to time sets 1 and 2 having significantly different means from time set 3. This expectation was based on the installation of scrubbers on the Kingston and Bull Run power plants and Figure 3.1. Overall these patterns were not noticed, the clearest evidence is the complete equality down the column of time sets 2 and 3 for  $SO_4^{2-}$  concentrations. Other outcomes were also unexpected such as pH always increasing over time and

the abnormal ANC concentrations. The decrease in ANC overtime as indicated in the Bonferroni figures was unexpected both because it is in contrast to the Julian date coefficients for ANC, which are mostly positive, and because pH is increasing over time. The Bonferroni method calculates significant means for the water quality variable, therefore the difference between the figures and the time trends suggest error in the trend analysis models.

The focus of this chapter was to investigate the decline in sulfur dioxide emissions from the Kingston and Bull Run power plants and how it may have impacted the decline in  $SO_4^{2-}$  concentrations in the through fall measurements of the Noland divide high elevation site. If a correlation existed it would be apparent in the pH results, but especially in the  $SO_4^{2-}$  results. A significant difference in means from time sets 3 to time sets 1 and 2 would support the hypothesis. The inequalities present between the time sets of pH data display a possible connection to the decline in sulfur dioxide pollution but there are many other factors that effect stream pH. The comparisons between the  $SO_4^{2-}$  sets are unfortunately mostly equal. This suggests  $SO_4^{2-}$  sequestration and a steady concentration being released into the steams which are being measured with grab samples. Until the sequestered pollution is depleted a significant difference in means may not be found.

## Chapter 4

# Power Analysis

## 4.1 Methods

#### 4.1.1 Introduction

The Park-wide park-wide stream survey has used elevation bands to further organize sites since its conception. The trend analysis of this paper along with past analyses have all determined trends within these bands, and the lack of high elevation sites brings the power of these trends into question. Power is the probability of correctly rejecting the false null hypothesis and is increased by minimizing error. An inherent amount of error comes with the hypothesis test of trend analysis preformed in chapter 2. Trend analysis tests the hypothesis that a trend exists in the data, which makes the null hypothesis one of no trend or a coefficient that equals zero. The error here is defined as type II error or  $\beta$  and can be seen in Table 4.1.  $\beta$  describes the failure to reject a false null hypothesis or in the case of this paper a failure to reject a "no trend" conclusion when there really is one. The opposite of  $\beta$  is the probability that a "no trend" conclusion will be rejected when a trend exists and is called the power of the test. A trend line with a power of 1.00 indicates a 100% chance that the calculated slope is not zero, a power of .50 means there is a 50% chance that the

calculated slope might not exist. Power indicates the reliability of the trends that are important in determining the health of streams in the GRSM.

Table 4.1: Hypothesis test results (Helsel and Hirsch, 1992)

		Unknown True Situation					
		$H_0$ is true	$H_0$ is false				
	Fail to	Correct decision	Type II error				
J	reject H <sub>0</sub>	Prob(correct decision) = $1-\alpha$	$Prob(Type II error) = \beta$				
Decision							
Dec	Daigat II	Type I error	Correct decision				
	Reject $H_0$	Prob (Type I error) = $\alpha$	Prob (correct decision) = $1-\beta$				
		Significance level	Power				

Power analysis refers to both post hoc and a priori analyses, in this paper both are completed with the help of the statistical program G\*power. It can compute both analyses for many different statistical tests, power analysis for regression was used here (Faul et al., 2009). All 144 trend lines from chapter 2 were evaluated using a post hoc analysis and also an a priori analysis to project the current park-wide stream survey program into the future. The two different power analyses are a rearrangement of the same method and have many similarities, but the post hoc analysis determines power while the a priori analysis determines number of observations. Post hoc of course is Latin for "after this" and is used to denote a power analysis after the completed trend analysis from chapter 2. A priori is Latin for "from the earlier" and specifies a power analysis used to set a desired power and calculate the number of observations from it.

A post hoc analysis was preformed for both of the Julian date coefficient tables from the step-wise equations in subsection 2.2.1 and the time variable equations in subsection 2.2.2, and are presented here in subsection 4.2.1. In contrast to the post hoc analysis the a priori analysis only needs to be calculated for each of the four

dependent variables. This is because for each analysis the three inputs (number of predictors, power, and ES) remain the same for each variable. The front analysis is only for one chosen power, and one chosen ES but G\*power will create a power graph which plots each power and the number of observations it needs. But this is where the analysis in G\*power ends and the results must be applied to the park-wide stream survey to get more specific results. This was accomplished in Excel, where the number of observations given by the power analysis were divided among the elevation bands. In this way elevation bands with many sites can be shown to contain more observations over time than necessary and elevation bands with lower amounts of sites are shown to need more observations for the same time period.

#### 4.1.2 Procedures

The most general power analysis methods originate from Jacob Cohen, who outlined his approach in" A Power Primer" (Cohen, 1992a). Cohen displayed ways to calculate the power for eight different tests the last of which is the F test for multiple and multiple partial correlation, which can be used for regression. The different tests are represented by their differences in calculating ES, which is described by Cohen as the probability to find a significant result (Cohen, 1992a). The equation for the ES of a regression model presented by Cohen is equal to the correlation coefficient divided by one minus the correlation coefficient.

$$ES = \frac{adj.r^2}{1 - adj.r^2} \tag{4.1}$$

This equation can be described as the ratio of explained to unexplained variation for the regression model. For the post hoc analysis this equation will be used to calculate a specific ES for each model from both methods of equations used for trend analysis in subsection 2.2.1 and subsection 2.2.2. The ES calculation is completed by G\*power after inputting the correlation coefficient (adj. r<sup>2</sup>).

#### Post hoc

G\*power uses ES along with the  $\alpha$  (.05) used for the regression model, the number observations, and number of predictors in the model to output the power of the F test for regression. This power will be between 0 and 1.00 and will be the power acquired by the models using past data and a calculated ES. With post hoc analysis, three of these inputs are passed from the output of the trend analysis: number of observations (N), adjusted  $r^2$  and number of predictors. The fourth input is ES or effect size which is calculated by G\*power before the study. A priori analysis also requires an ES value but it is chosen, instead of calculated, along with the power. Just like the post hoc analysis the number of predictors is still needed for the a priori analysis and taken from the number of predictors given in the step-wise analysis in Table 2.1.

#### A priori

The a priori analysis is more conditional than the straight forward calculations for the post hoc analysis. Instead of outputting a power value like the post hoc analysis,  $G^*$  power will compute the number of observations for a given scenario. The inputs for this study are  $\alpha$  (.05), desired power, number of predictors, and ES. All of these inputs can be changed or manipulated based on the anticipated outcome. For this analysis the assumption was made that the same trend analysis as the one completed in chapter 2 would be attempted in the future. Based on this assumption the same step-wise equations constructed in Table 2.1 can be used to help chose the number of predictors and  $\alpha$ .

The most encompassing way to present an a priori analysis is through a power graph. The power graphs plot power on the y-axis and number of observations on the x-axis. Using this as a tool a planner can choose a desired power and get the corresponding number of observations.

Choosing an ES value and desired power will be a matter of convention. To make choosing the ES value easier Cohen has defined small, medium, and large ES values for each of the eight tests described in Cohen (1992a). Concerning the multiple and multiple partial correlation test he decided on .02, .15, and .35 respectively. All of these ES values can be graphed in the power graphs by plotting different ES values as curves on the same plot. But in order to later determine more efficient site counts per elevation band a best ES value must be chosen. An ES value of .15 was settled upon after the power graphs for all three conventions per dependent variable were made. .02 was too small, requiring very high numbers of observations to reach a decent power. ES values of .35 can acquire small numbers of observations thus achieving a decent power level easier, but the smaller the ES the better. .15 is less than half of .35 so it minimizes the chances for insignificant results and the numbers of observations are reasonable to reach higher powers. If no argument can be made for any other desired power then Cohen suggests .80. This is chosen for its reasonable ratio of Type I error to Type II error which reflects their importance. If the power is .80 then  $\beta = .20$  and  $\alpha = .05$  and this makes the Type II error four times as likely as Type I error (Cohen, 1992b).

## 4.2 Results

### 4.2.1 Post hoc

The results of the post hoc analysis on both the step-wise method trend analyses and the time variable trend analysis are reported in subsection 4.2.1. They are broken into the four water quality variables (pH, ANC, NO<sub>3</sub>, SO<sub>4</sub>) and divided into the tree time sets (93-02, 03-08, 09-12), and then further divided into the six elevation classes. Each time trend from chapter 2 is described by its number of observations, the adjusted  $r^2$ , the calculated ES, and finally their observed power. Of the 72 lines evaluated for power from step-wise trend analysis (subsection 2.2.1) only eight of them were less than 1.00 and only two were insignificant. One of the insignificant trends was the trend for Nitrate, set 3, class 5, and along with insignificance, the

Table 4.2: pH Step-Wise Post Hoc Power Analysis Results

Set	Class	N	Adjusted $r^2$	Effect Size	Actual Power
	1	327	0.712	2.47	1.00
0.5	2	393	0.388	0.63	1.00
1993-2002	3	400	0.693	2.26	1.00
993	4	121	0.205	0.26	0.99
1.0	5	116	0.165	0.20	0.96
	6	110	0.505	1.02	1.00
	1	255	0.781	3.57	1.00
08	2	289	0.348	0.53	1.00
2003-2008	3	299	0.663	1.97	1.00
03	4	119	0.400	0.67	1.00
20	5	35	0.300	0.43	0.74
	6	97	0.317	0.46	1.00
	1	191	0.894	8.43	1.00
12	2	212	0.606	1.54	1.00
-20	3	228	0.766	3.27	1.00
2009-2012	4	97	0.593	1.46	1.00
20	5	29	0.158	0.19	0.28
	6	76	0.286	0.40	0.99

Table 4.3: ANC Step-Wise Post Hoc Power Analysis Results

Set	Class	N	Adjusted r <sup>2</sup>	Effect Size	Actual Power
	1	327	0.985	65.67	1.00
0.5	2	392	0.603	1.52	1.00
-20	3	398	0.971	33.48	1.00
1993-2002	4	120	0.709	2.44	1.00
1.0	5	116	0.760	3.17	1.00
	6	110	0.802	4.05	1.00
	1	255	0.996	249.00	1.00
80	2	289	0.779	3.52	1.00
2003-2008	3	299	0.996	249.00	1.00
03-	4	119	0.779	3.52	1.00
20	5	35	0.739	2.83	1.00
	6	97	0.812	4.32	1.00
	1	191	0.989	89.91	1.00
12	2	212	0.862	6.25	1.00
-20	3	228	0.997	332.33	1.00
2009-2012	4	97	0.772	3.39	1.00
20	5	29	0.540	1.17	0.96
	6	76	0.809	4.24	1.00

 Table 4.4: Nitrate Step-Wise Post Hoc Power Analysis Results

Set	Class	N	Adjusted r <sup>2</sup>	Effect Size	Actual Power
	1	275	0.503	1.01	1.00
2	2	$\frac{275}{377}$	0.699	2.32	1.00
1993-2002	3	365	0.359	0.56	1.00
-56	4	105	0.410	0.69	1.00
10	5	66	0.328	0.49	0.98
	6	81	0.871	6.75	1.00
	1	252	0.551	1.23	1.00
08	2	296	0.816	4.43	1.00
2003-2008	3	297	0.637	1.75	1.00
03	4	121	0.405	0.68	1.00
20	5	30	0.562	1.28	0.98
	6	98	0.832	4.95	1.00
	1	191	0.376	0.60	1.00
12	2	212	0.735	2.77	1.00
-20	3	228	0.598	1.49	1.00
2009-2012	4	97	0.635	1.74	1.00
20	5	29	-0.272	NA	NA
	6	76	0.881	7.40	1.00

 Table 4.5:
 Sulfate Step-Wise Post Hoc Power Analysis Results

Set	Class	N	Adjusted r <sup>2</sup>	Effect Size	Actual Power
-	1	325	0.569	1.32	1.00
02	$\overset{-}{2}$	390	0.766	3.27	1.00
1993-2002	3	391	0.590	1.44	1.00
993	4	119	0.402	0.67	1.00
1.0	5	116	0.566	1.30	1.00
	6	110	0.716	2.52	1.00
	1	261	0.673	2.06	1.00
08	2	298	0.893	8.35	1.00
2003-2008	3	308	0.923	11.99	1.00
03	4	123	0.343	0.52	1.00
20	5	37	0.884	7.62	1.00
	6	101	0.844	5.41	1.00
	1	190	0.536	1.16	1.00
12	2	212	0.887	7.85	1.00
-20	3	228	0.915	10.76	1.00
2009-2012	4	97	0.529	1.12	1.00
20	5	29	0.658	1.92	1.00
	6	76	0.861	6.19	1.00

 ${\bf Table\ 4.6:\ pH\ Time\ Variable\ Post\ Hoc\ Power\ Analysis\ Results}$ 

Set	Class	N	Adjusted r <sup>2</sup>	Effect Size	Actual Power
	1	327	0.047	0.049	0.93
02	2	393	0.128	0.15	1.00
-20	3	400	0.013	0.01	0.46
1993-2002	4	121	0.059	0.06	0.61
1:0	5	116	0.051	0.05	0.52
	6	110	0.096	0.11	0.81
	1	255	0.040	0.04	0.78
08	2	289	0.061	0.06	0.96
2003-2008	3	299	0.020	0.02	0.52
03	4	119	0.148	0.17	0.97
20	5	35	-0.069	NA	NA
	6	97	0.081	0.09	0.67
	1	191	0.028	0.03	0.47
12	2	212	0.052	0.05	0.82
-20	3	228	-0.009	NA	NA
2009-2012	4	97	0.200	0.25	0.99
20	5	29	0.218	0.28	0.58
	6	76	0.039	0.04	0.27

Table 4.7: ANC Time Variable Post Hoc Power Analysis Results

~					
Set	Class	N	Adjusted r <sup>2</sup>	Effect Size	Actual Power
	1	327	$\boldsymbol{0.024}$	0.02	0.65
02	2	392	0.189	0.23	1.00
-20	3	398	0.000	0.00	0.06
1993-2002	4	120	0.294	0.42	1.00
16	5	116	0.381	0.62	1.00
	6	110	0.075	0.08	0.69
	1	255	0.001	0.00	0.07
80	2	289	0.081	0.09	0.99
2003-2008	3	299	-0.003	NA	NA
03-	4	119	0.180	0.22	0.99
20	5	35	0.337	0.51	0.93
	6	97	0.094	0.10	0.74
	1	191	0.000	0.00	0.05
12	2	212	0.056	0.06	0.85
-20	3	228	-0.002	NA	NA
2009-2012	4	97	0.161	0.19	0.96
20	5	29	0.466	0.87	0.98
	6	76	0.058	0.06	0.39

Table 4.8: Nitrate Time Variable Post Hoc Power Analysis Results

Set	Class	N	Adjusted $r^2$	Effect Size	Actual Power
	1	275	0.016	0.02	0.39
03	2	377	0.017	0.02	0.55
-20	3	365	-0.004	NA	NA
1993-2002	4	105	-0.027	NA	NA
1.0	5	66	0.120	0.14	0.68
	6	81	0.092	0.10	0.64
	1	252	0.061	0.06	0.94
08	2	296	0.043	0.04	0.87
2003-2008	3	297	-0.003	NA	NA
03	4	121	0.086	0.09	0.80
20	5	30	-0.082	NA	NA
	6	98	0.046	0.05	0.40
	1	191	0.018	0.02	0.31
12	2	212	0.011	0.01	0.22
-20	3	228	-0.004	NA	NA
2009-2012	4	97	-0.016	NA	NA
20	5	29	-0.039	NA	NA
	6	76	-0.016	NA	NA

 Table 4.9: Sulfate Time Variable Post Hoc Power Analysis Results

Set	Class	N	Adjusted $r^2$	Effect Size	Actual Power
	1	325	0.045	0.05	0.92
02	2	390	0.009	0.01	0.32
-20	3	391	-0.004	NA	NA
1993-2002	4	119	-0.016	NA	NA
10	5	116	-0.010	NA	NA
	6	110	-0.009	NA	NA
	1	261	0.043	0.04	0.82
08	2	298	0.014	0.01	0.37
2003-2008	3	308	0.006	0.01	0.18
03	4	123	0.023	0.02	0.26
20	5	37	-0.024	NA	NA
	6	101	0.074	0.08	0.64
	1	190	0.005	0.01	0.11
12	2	212	-0.010	NA	NA
-20	3	228	-0.007	NA	NA
2009-2012	4	97	-0.011	NA	NA
20	5	29	-0.076	NA	NA
	6	76	0.007	0.01	0.08

adjusted  $r^2$  was negative (-0.272) and therefore the power could not be found. The other insignificant trend was pH, set 3, class 5, which received the lowest observed power of .28.

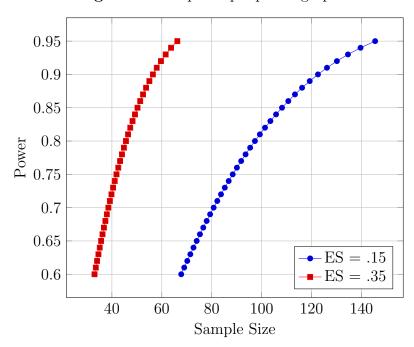
In large dissimilarity from the step-wise trend models, 52 of the 72 trends from the trends using the time variable equations (subsection 2.2.2) were insignificant. Of the 20 significant trends observed powers range from .26 to 1.00, 11 of them are above .80 and 2 are .99 or greater. The power of an insignificant trend line is useless.

## 4.2.2 A priori

### Power graphs

The traditional presentation for an a priori power analysis is the power graph. Here the powers lie on the y-axis while the number of observations lie on the x-axis. All of the water quality variables and the time model get their own graph except for ANC and NO<sub>3</sub>, which are the same because they contain the same number of predictors from their step-wise model. On each graph two curves are plotted representing an ES of either .15 or .35, they all rise from (0, 0) asymptotically towards a power of 1.00. Despite the similar shapes, the more predictors a model has, the greater number of observations it needs to reach equal powers, the power graph for sulfate (Figure 4.3) needs almost 30 more samples than the power graph for time variables (Figure 4.4) to reach a power of .80 with an ES of .15.

Figure 4.1: A priori pH power graph



**Figure 4.2:** A priori ANC and Nitrate Power Graph. The power graphs for ANC and Nitrate are the same because they both have the same number of predictors.

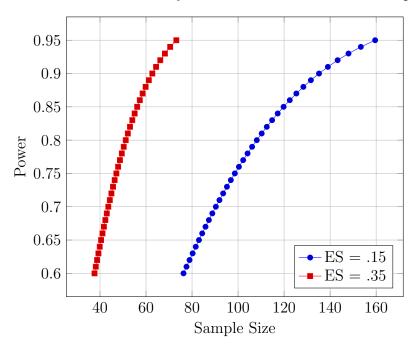


Figure 4.3: A priori Sulfate Power Graph

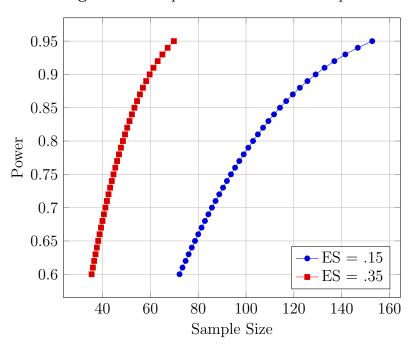
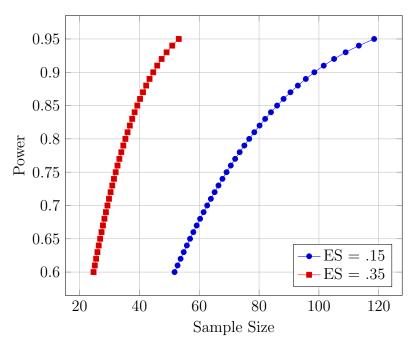


Figure 4.4: A prioir Time Variables Power Graph



**Table 4.10:** A priori calculation in G\*power when alpha, ES, and power are set to .05, .15, and .80 respectively.

	Number of predictors	$N_a$
рН	6	98
ANC	8	109
Nitrate	8	109
Sulfate	7	103
Time	3	77

#### A priori manipulation

The results of the a priori analysis are presented in Table 4.10 but are inconvenient and require manipulation in order to apply them to the park-wide stream survey. There are two different ways for the researcher to achieve these results with a focus on time: by adjusting the frequency of collection or by adding sites. Both methods can be used to quickly acquire enough observations (samples) required by Table 4.10 to have a powerful trend analysis. But adding sites is cheaper and can solve the poor elevational distribution of the sites in the park-wide stream survey.

The a priori power analysis can be manipulated to calculate a number of sites per elevation band for the park-wide stream survey in the GRSM. First, samples per year per elevation band are counted for the 2012 year and will be represented by n. Next the results from Table 4.10 are divided by samples per year per elevation band to get the number of years it will take, at the 2012 sampling rate, to reach a power of .80.

$$yrs. = \frac{N_a}{n} \tag{4.2}$$

However, in order to get to the number of sites per elevation band needed to reach a power of .80, the years will have to be held constant. If the future trend analysis is to be completed using the equation with only time variables (instead of the step-wise equations) then 77 samples will need to be collected in one year to reach a power

of .80 according to Table 4.10. But if the future trend analysis is to be completed using the step-wise equations from Table 2.1 then at least 109 samples will need to be collected in one year to satisfy the requirements for ANC and NO<sub>3</sub>. For the step-wise equations N will be rounded up to 110 and labeled  $N_b$ .

**Table 4.11:** Samples/year/equation to achieve a power .80  $(N_b)$ 

Equation	1	2	3	4
Water Quality Variables	110	55	37	28
Time Variables	77	39	26	19

The number of observations required per year per equation are presented in Table 4.11, which has been calculated out to four years. Instead of completing the trend analysis after one year, one could wait four years and only need to collect 28 samples per year. Subtracting the number of samples collected in one year per elevation band in 2012 from the number of samples needed to be collected per year to reach a power of .80 will provide the number of samples needed per elevation band to receive a power of .80  $(N_c)$ .

$$N_c = N_b - n \tag{4.3}$$

To get an estimation for the number of sites needed per elevation band to achieve a power of .80, the number of samples needed per elevation band to receive a power of .80  $(N_c)$  were divided by six which is number of times each site is sampled per year.

$$#Sites = \frac{N_c}{6} \tag{4.4}$$

This scenario was followed through with both methods of trend lines. Table 4.12 records the six elevation bands along with the site numbers that belong to them. In the column labeled, current n per year, the amount of samples collected per elevation band in the year 2012 are tabulated. Then using Equation 4.2 the number of years needed for each variable to reach a power of .80 is calculated. Looking at the table

**Table 4.12:** Years to achieve a power of .80

Elevation Bands	Site #	Current n/yr	рН	ANC NO <sub>3</sub>	$SO_4$	Time variables
1	13 ,23, 24, 30, 479	26	3.77	4.19	3.96	2.96
2	4, 311, 268, 480, 310,	34	2.88	3.21	3.03	2.26
3	483, 147, 148, 484 114, 481, 482, 149, 66, 492, 137, 293, 270, 493, 485, 144, 224	62	1.58	1.76	1.66	1.24
4	143, 142, 73, 71	24	4.08	4.54	4.29	3.21
5	74, 221, 251, 233	22	4.45	4.95	4.68	3.50
6	253, 234	12	8.17	9.08	8.58	6.42

there are 26 samples collected in elevation band one in one year. In order to compute a trend line for pH using the same step-wise model from Table 2.1 that receives a power of .80, samples would need to be collected for 3.77 years before the trend line can be computed. The longest waiting period is for ANC or NO<sub>3</sub> at elevation class six which requires 9.08 years, presumably because they have the highest number of predictors and elevation class six includes only two sites.

**Table 4.13:** Necessary sites scenario for water quality variables

	#Samples required				# sites required			
Elevation Bands	1 yr	2 yrs	3 yrs	4 yrs	1 yr	2 yrs	3  yrs	4 yrs
1	84	29	11	2	14	5	2	0
2	76	21	3	-7	13	4	0	-1
3	48	-7	-25	-35	8	-1	-4	-6
4	86	31	13	4	14	5	2	1
5	88	33	15	6	15	6	2	1
6	98	43	25	16	16	7	4	3

Tables Table 4.13 and Table 4.14 correspond to both methods of trend analysis, the step-wise equations and the time variables equations. Both tables are broken down into two sides, the left side contains number of samples while the right side contains number of sites. Then each side is arranged by elevation band and calculated out

Table 4.14: Necessary sites scenario for time variables

	#Samples required				# sites required			
Elevation Bands	1 yr	2 yrs	3 yrs	4 yrs	1 yr	2 yrs	3 yrs	4 yrs
1	51	13	0	-7	9	2	0	-1
2	43	5	-8	-15	7	1	-1	-2
3	15	-24	-36	-43	3	-4	-6	-7
4	53	15	2	-5	9	2	0	-1
5	55	17	4	-3	9	3	1	0
6	65	27	14	7	11	4	2	1

to four years. Equation 4.3 is used to calculate the number of samples required and then these numbers are divided by six to get the number of sites. The numbers on the right side of the tables represent the change to the current number of sites in that elevation band needed to achieve a power of .80 with an ES of .15 using the same models from chapter 2. In Table 4.13 for elevation class 3, 48 more samples need to be collected if a trend line for the water quality dependents with a power of .80 is to be created after one year. But if a trend line can wait to be created after two years, then there is a surplus of seven samples per year. If four years can be waited there is a surplus of 35 samples which on the right side of the table translates into a surplus of 6 whole site locations per year.

## 4.3 Discussion and Conclusions

#### Post hoc

Step-wise equations By reviewing the results of the post hoc analysis after an a priori analysis has been completed it is easier to see why the results were outstanding for the step-wise equations and awful for the time based equations. Knowing that an a priori analysis on the step-wise equations will produce a requirement of 110 observations for a power of .80 and an ES of .15 from Table 4.10, it can easily be recognized that as the number of observations in the results for the post-hoc power

analysis on trends calculated using the step-wise equations (subsection 4.2.1) decline from 110 the power also declines. In concert with the large number of observations, the observed ES values are very large compared to the chosen ES of .15 which coincides with the observed powers being close to 1.00. The large conventional ES given by Cohen is .35 and only 3 of the trend lines analyzed here were below that, all in pH. And because the ES is a ratio of the adjusted r<sup>2</sup> the ES declines as the r<sup>2</sup> does, the higher the r<sup>2</sup> the better. But for a calculated ES of .15 the adjusted r<sup>2</sup> doesn't need to be very high. For example, the analyzed trend line for pH in time set 3 elevation class 5 has an adjusted r<sup>2</sup> of .158 and the ES is .19, which is larger than .15. Assuming that a power of .80 and an ES of .15 is ideal, then this post hoc analysis uses too many observations. One way to have fewer observations would be to use fewer years in the study. Another way would be to use less sites in the survey.

Time variable based equations The two post hoc analyses on the two different models varied considerably. The differences in powers between the two cannot be caused by a lower number of observations because the number of observations used in both are the same. But they can be accounted for by the low adjusted r<sup>2</sup> values, which are very low for the results for the time variable equations (subsection 2.2.2), and leads to the low ES values. Overlooking the fact that most of the regression models for the time variable analysis are insignificant, most of the powers calculated from subsection 2.2.2 are not too low. Of the 20 significant lines eleven have a power equal to or above .80.

#### A priori

The a priori power graphs themselves show every possible power and the number of observations needed to achieve it. However, they are based on the particular stepwise equations that were created using this particular dataset. Since the step-wise process uses past data to create the equations, every time new data is added the equations could change. The a priori analysis assumes that these same equations,

with the same number of variables, will be used to detect trends in the future. But even if the number of sites remain the same past this point, the data will still be different. And if the site numbers do change, such as more sites are added to the upper elevations and sites are removed from the lower elevations, then the step-wise equations are at greater risk of changing. Then if the number of predictors changes because the data changed this a priori analysis would not be applicable. A more static set of equations would ease this pressure.

These power graphs can still be used by managers and planners as an educated guess. After the number of observations for a desired power is determined from the graphs the observations can be placed into the survey with efficiency in mind. All chosen power and ES values can represent a different scenario. One such scenario was carried out for a power of .80 and an ES of .15. Although any value in the power graphs can be chosen these values were chosen as the most efficient.

The results of this scenario can solve two concerns of the survey, the lack of high elevation sites and the lack of funding. By following the results in Table 4.13, waiting a minimum of four years before the next trend analysis can lead to the removal of two sites from the survey. And assuming that cost of the survey is related to the number of sites, then removing sites will save money. But removing two sites is just the sum difference of a redistribution suggested by the scenario. In fact, one site should be removed from elevation class 2 and six from elevation class 3. One site each need to be added to classes 4 and 5 and three sites should be added to class 6. There are too many sites in the lower elevation classes of 2 and 3 and not enough sites in the higher elevation classes of 4, 5, and 6. A redistribution of sites is in order.

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# Appendix

# Appendix A

Site Data

### A.1 Site Data

Table A.1: GRSM Stream Survey site descriptions

	Site ID	Site Description	Watershed
1	173	Mill Creek above Abrams Creek	Abrams
2	174	Abrams Creek below Cades Cove	Abrams
3	488	Mill Creek at Pumphouse on Forge Creek Road	Abrams
4	489	Abrams Creek 300 m below trailhead bridge	Abrams
5	142	Beech Creek above Lost Bottom Creek	Cataloochee
6	143	Lost Bottom Creek (Cataloochee Creek)	Cataloochee
7	144	Palmer Creek above Pretty Hollow Creek	Cataloochee
8	147	Lower Cataloochee Creek	Cataloochee
9	148	Lower Little Cataloochee Creek	Cataloochee
10	149	Middle Cataloochee Creek at bridge	Cataloochee
11	293	Rough Fork at Caldwell House	Cataloochee
12	493	Palmer Creek at Davidson Branch Trail	Cataloochee
13	4	Lower Rock Creek	Cosby
14	114	Cosby Creek at log bridge	Cosby
15	137	Upper Rock Creek (Cosby Creek)	Cosby
16	492	Camel Hump Creek off Low Gap Trail	Cosby
17	221	Hazel Creek above cascades	Hazel
18	224	Hazel Creek just below Proctor Creek Confluence	Hazel
19	310	Bone Valley Creek (Hazel Creek)	Hazel
20	311	Hazel Creek below Haw Gap Creek	Hazel
21	479	Hazel Creek at Campsite 86	Hazel
22	480	Haw Gap Creek at bridge near Campsite 84	Hazel
23	481	Little Fork above Sugar Fork Trail	Hazel
$^{24}$	482	Sugar Fork above Little Fork	Hazel
25	483	Sugar Fork above Haw Gap Creek	Hazel
26	484	Hazel Creek at Cold Spring Gap Trail	Hazel
27	485	Walker Creek above Hazel Creek Trail	Hazel
28	13	Little River at boundary	Little
29	23	Lower Middle Prong Little River	Little
30	24	Lower West Prong Little River	Little
31	30	West Prong Little Pigeon at Headquarters	Little
32	66	West Prong Little Pigeon at Chimneys Picnic Area	Little
33	71	Road Prong above barrier cascade	Little
34	73	Walker Camp Prong above Road Prong	Little
35	74	Walker Camp Prong above Alum Cave Creek	Little
36	233	Walker Camp Prong above Alum Cave	Little
37	234	Upper Road Prong	Little
38	237	Walker Camp Prong at last bridge	Little
39	251	Beech Flats above US 441 loop	Oconaluftee
40	252	Beech Flats below roadcut	Oconaluftee
41	253	Beech Flats above roadcut	Oconaluftee
42	268	Oconaluftee River below Smokemont	Oconaluftee
43	270	Beech Flats at Kephart Footbridge	Oconaluftee

Table A.2: GRSM site data continued

	Site ID	Elevation (ft)	Elevation (m)	slope	Latitude	Longitude	Historical Elevation Classes	New elevation classes
1	173	1715	522.73	35.68	35.59104	-83.85361	3	3
2	174	1715	522.73	10.27	35.59186	-83.85308	3	3
3	488	1790	545.59	4.04	35.58349	-83.83446	4	1
4	489	1710	521.21	32.78	35.59145	-83.85397	4	1
5	142	3300	1005.84	32.42	35.63565	-83.14537	5	2
6	143	3280	999.74	35.69	35.63625	-83.14481	6	2
7	144	2990	911.35	35.66	35.63900	-83.13078	5	2
8	147	2460	749.81	16.84	35.66688	-83.07277	4	3
9	148	2475	754.38	7.58	35.66913	-83.07283	4	3
10	149	2550	777.24	4.45	35.64627	-83.07554	5	3
11	293	2755	839.72	18.73	35.62442	-83.11391	5	4
12	493	2840	865.63	33.10	35.63462	-83.11943	6	6
13	4	2080	633.98	6.11	35.76133	-83.21044	3	1
14	114	2510	765.05	13.71	35.74863	-83.20066	5	2
15	137	2750	838.20	22.92	35.74616	-83.21630	5	2
16	492	2730	832.10	25.86	35.74457	-83.19876	5	6
17	221	4000	1219.20	30.02	35.54632	-83.58283	8	3
18	224	2999	914.00	17.92	35.53212	-83.62234	6	3
19	310	2240	682.75	19.63	35.49994	-83.68014	4	4
20	311	2155	656.84	26.20	35.49377	-83.68852	4	5
21	479	1740	530.35	39.70	35.47233	-83.71933	3	5
22	480	2201	671.00	10.07	35.49474	-83.68873	4	5
23	481	2540	774.19	30.90	35.50256	-83.70835	5	5
24	482	2540	774.19	38.66	35.50236	-83.70859	5	6
25	483	2320	707.14	34.29	35.49947	-83.69494	4	6
26	484	2475	754.38	9.11	35.50331	-83.65930	5	1
27	485	2860	871.73	5.17	35.52249	-83.63101	6	1
28	13	1100	335.28	44.21	35.66763	-83.71450	2	1
29	23	1150	350.52	5.96	35.65724	-83.70979	2	1
30	24	1150	350.52	31.60	35.65682	-83.71017	2	1
31	30	1430	435.86	2.17	35.68819	-83.53672	2	1
32	66	2680	816.86	17.92	35.63723	-83.49484	5	2
33	71	3400	1036.32	31.28	35.63440	-83.47032	6	2
34	73	3360	1024.13	28.98	35.63476	-83.46931	6	2
35	74	3820	1164.34	18.07	35.62912	-83.45102	7	2
36	233	4255	1296.92	21.86	35.61830	-83.42718	8	3
37	234	5000	1524.00	23.93	35.60975	-83.45043	10	3
38	237	4520	1377.70	30.21	35.62409	-83.41692	9	3
39	251	4010	1222.25	19.03	35.60226	-83.41533	8	3
40	252	4680	1426.46	33.32	35.60666	-83.43391	9	3
41	253	4760	1450.85	26.42	35.60682	-83.43510	9	3
42	268	2169	661.00	3.31	35.55293	-83.30937	4	4
43	270	2799	853.00	22.92	35.58641	-83.36400	5	4

# Appendix B

**Descriptive Statistics** 

# B.1 pH

 Table B.1: pH Descriptive Statistics

Set	Class	Elevation m (ft)	N	Minimum	Maximum	Mean
	1	304.8-609.6 (1000-2000)	327	4.96	7.90	6.57
02	2	609.6-762 (2000-2500)	393	5.32	7.00	6.25
1993-2002	3	762-914.4 (2500-3000)	400	4.65	8.24	6.44
93	4	914.4-1066.8 (3000-3500)	121	6.18	7.11	6.50
10	5	1066.8-1371.6 (3500-4500)	116	6.07	7.05	6.50
	6	1371.6 < (4500 <)	110	5.77	7.06	6.41
	1	304.8-609.6 (1000-2000)	255	5.22	7.95	6.65
08	2	609.6-762 (2000-2500)	289	4.83	7.07	6.32
2003-2008	3	$762-914.4 \ (2500-3000)$	299	4.65	8.10	6.55
003	4	914.4-1066.8 (3000-3500)	119	5.95	7.06	6.58
20	5	1066.8-1371.6 (3500-4500)	35	5.98	7.03	6.50
	6	1371.6 < (4500 <)	97	5.79	7.05	6.44
	1	304.8-609.6 (1000-2000)	191	5.42	8.02	6.77
12	2	609.6-762 (2000-2500)	212	4.91	7.28	6.47
-20	3	$762-914.4 \ (2500-3000)$	228	4.73	7.96	6.68
2009-2012	4	914.4-1066.8 (3000-3500)	97	6.20	7.08	6.68
20	5	1066.8-1371.6 (3500-4500)	29	6.30	7.11	6.77
	6	1371.6 < (4500 <)	76	4.24	7.09	6.52

### B.2 ANC

Table B.2: ANC Descriptive Statistics

Set	Class	Elevation m (ft)	N	Minimum	Maximum	Mean
	1	304.8-609.6 (1000-2000)	327	-20.74	1534.47	149.76
02	2	609.6-762 (2000-2500)	392	-7.43	182.95	40.75
993-2002	3	762-914.4 (2500-3000)	398	-19.97	1624.49	158.44
933	4	914.4-1066.8 (3000-3500)	120	24.45	178.00	75.84
100	5	1066.8-1371.6 (3500-4500)	116	41.34	162.76	77.06
	6	1371.6 < (4500 <)	110	15.64	165.02	68.01
	1	304.8-609.6 (1000-2000)	255	-37.09	1314.56	173.48
80	2	609.6-762 (2000-2500)	289	-1.88	145.95	42.20
-20	3	762-914.4 (2500-3000)	299	-26.45	1591.06	172.82
2003-2008	4	914.4-1066.8 (3000-3500)	119	23.36	128.28	69.90
30	5	1066.8-1371.6 (3500-4500)	35	36.37	115.80	77.84
	6	1371.6 < (4500 <)	97	6.73	130.63	55.68
	1	304.8-609.6 (1000-2000)	191	-0.02	1377.93	164.72
12	2	609.6-762 (2000-2500)	212	-11.74	174.52	44.45
-20	3	762-914.4 (2500-3000)	228	-18.28	1535.69	160.14
2009-2012	4	914.4-1066.8 (3000-3500)	97	25.70	107.58	64.13
20	5	1066.8-1371.6 (3500-4500)	29	40.10	115.94	73.55
	6	1371.6 < (4500 <)	76	-3.92	114.28	46.15

### B.3 Nitrate

Table B.3: Nitrate Descriptive Statistics

Set	Class	Elevation m (ft)	N	Minimum	Maximum	Mean
	1	304.8-609.6 (1000-2000)	275	0.00	49.94	12.04
02	2	609.6-762 (2000-2500)	377	1.37	73.76	26.62
993-2002	3	762-914.4 (2500-3000)	365	0.00	96.13	26.14
993	4	914.4-1066.8 (3000-3500)	105	2.16	28.29	11.90
1:0	5	1066.8-1371.6 (3500-4500)	66	1.23	10.55	4.35
	6	1371.6 < (4500 <)	81	1.56	60.46	21.13
	1	304.8-609.6 (1000-2000)	252	0.50	62.75	16.56
08	2	609.6-762 (2000-2500)	296	0.62	67.12	29.20
2003-2008	3	762-914.4 (2500-3000)	297	0.13	95.72	27.69
03	4	914.4-1066.8 (3000-3500)	121	1.87	55.67	17.51
20	5	1066.8-1371.6 (3500-4500)	30	1.45	26.48	7.59
	6	1371.6 < (4500 <)	98	1.09	72.79	24.88
	1	304.8-609.6 (1000-2000)	191	0.22	62.14	16.31
12	2	609.6-762 (2000-2500)	212	4.43	72.17	30.08
-20	3	$762-914.4 \ (2500-3000)$	228	1.04	72.16	26.23
2009-2012	4	914.4-1066.8 (3000-3500)	97	0.54	34.67	18.72
20	5	1066.8-1371.6 (3500-4500)	29	0.21	83.68	6.44
	6	1371.6 < (4500 <)	76	0.16	79.04	32.17

### B.4 Sulfate

Table B.4: Sulfate Descriptive Statistics

Set	Class	Elevation m (ft)	N	Minimum	Maximum	Mean
03	1	304.8-609.6 (1000-2000)	325	12.32	85.01	36.09
	2	609.6-762 (2000-2500)	390	0.00	159.51	51.68
993-2002	3	762-914.4 (2500-3000)	391	0.00	262.37	54.00
993	4	914.4-1066.8 (3000-3500)	119	12.34	77.74	25.16
13	5	1066.8-1371.6 (3500-4500)	116	7.51	79.98	26.14
	6	1371.6 < (4500 <)	110	14.71	61.16	28.35
	1	304.8-609.6 (1000-2000)	261	10.00	93.23	38.85
08	2	609.6-762 (2000-2500)	298	11.64	152.55	48.19
2003-2008	3	762-914.4 (2500-3000)	308	10.44	490.01	54.25
03	4	914.4-1066.8 (3000-3500)	123	13.88	61.31	29.04
20	5	1066.8-1371.6 (3500-4500)	37	12.18	117.46	30.54
	6	1371.6 < (4500 <)	101	10.02	65.53	34.31
	1	304.8-609.6 (1000-2000)	190	14.61	113.83	39.63
12	2	609.6-762 (2000-2500)	212	13.45	125.36	47.41
2009-2012	3	$762-914.4 \ (2500-3000)$	228	13.59	317.63	58.15
.600	4	914.4-1066.8 (3000-3500)	97	19.89	46.66	29.33
20	5	1066.8-1371.6 (3500-4500)	29	16.78	109.18	36.16
	6	1371.6 < (4500 <)	76	15.72	63.32	37.05

# Vita

Tim Pobst was born in Nashville, TN on June 1st 1985 to George and Peggy Pobst. He graduated from Centennial High School near Franklin, TN and was accepted to the University of Tennessee immediately after. He was undecided for three years before deciding to try for a civil engineering degree and he finished it in spring of 2011. He stayed at the University of Tennessee to get a masters degree in environmental engineering under Dr. Schwartz.