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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

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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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Dr. Schwartz, Keil Neff, Matt Kulp, and Steve Moore.

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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 Stream Survey program since 1993. Stream health is determined by statistical analysis on water quality constituents such as pH, ANC, Nitrate, and Sulfate. In 2002 Robinson et al. (2008) found negative pH time trends, while more recently Meijun Cai (2013) 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 Meijun Cai (2013) 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 furthur study the apparent correlation. Currently elevation in the Stream 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 Stream 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. Then a power analysis is 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 Meijun Cai (2013). 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 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 distribution of sites.

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Chapter 1

Introduction

1.1 Description of study area

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). 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. Acid deposition negatively affects the 3,000 km of streams present in the GRSM, impacting every living organism in the park that relies on its water quality.

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). These three weather

modes transport and deposit the pollution of the industrialized world all over the rest of the world. The top contributor of manmade pollution to acid deposition is fossil fuel combustion, such as gas engines for transportation, and industrial plants for production and power. 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 (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). Acid deposition will acidify the surface waters, which can harm anything that interacts with it, including the soils, life forms and streams. The rate of stream acidification can be slowed by the alkalinity of the water that is measured by ANC (acid neutralizing capacity) and is related to the amount of bases present in the water. The base cations that buffer against acidification can also be depleted through leaching, which is also caused by acid increase. In this process, the inherent base cation minerals react and run out leaving excess H⁺ and Al to be released into the water (Sullivan et al., 2004). The increase of H⁺ concentration caused by leaching will lower the pH, and Al can be toxic to fish (Driscoll et al., 2003). A constant removal of base cations can lead to chronic acidification by permanently low ANC.

Acidification of bodies of water 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. 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 (Robinson et al., 2008).

1.3 The Stream Survey

The 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. It collects grab samples many times per year from multiple sites in order to monitor the health of the streams in the park. There are nearly 500 sites listed in the stream survey, but the number of sites monitored has dwindled to the 43 sites examined in this paper. Currently, samples are collected from 32 sites every two months and an additional 11 samples are collected twice per year. These samples cover streams from 6 GRSM stream systems. Every sample is measured for pH, ANC, conductivity, acid anions (CL⁻, SO₄², NO₃⁻, ammonia (NH₄⁺)), the base cations (Ca²⁺, Mg²⁺, K⁺, Na⁺), and dissolved metals (Al, Cu, Fe, Mn, Si and Zn). A ManTechTM autotitrator was used for pH, ANC, and conductivity. A DionexTM ion chromatograph (IC) was used for the analysis of CL⁻, SO₄²⁻, NO₃⁻, and NH₄⁺. A Thermo-ScientificTM Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) was used for the study of Ca²⁺, Mg²⁺, Na⁺, K⁺, Al, Cu, Fe, Mn, Si and Zn.

1.3.1 Database

All data is collected, under contract, for the NPS. Sample identifiers such as time, place, pH, and constituent concentrations are aggregated in spreadsheets and formatted to NPS specifications. 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.

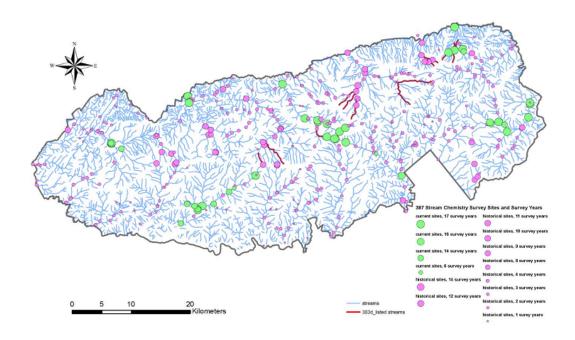


Figure 1.1: Site locations for the Stream Survey from 1993 to 2009.

The database is dynamic and changes along with the stream survey, theory, and lab techniques and tools. Currently, the collection, analysis, and formatting falls under Dr. Schwartz of the University of Tennessee Civil and Environmental Engineering Department. He inherited it from Dr. Robinson of the same department, who inherited it from the Forestry Department. A difference in analysis and formatting methods between the two departments is obvious in the data. There are many more outliers present in the data curated by the Forestry Department, which makes smoothing and statistically analyzing that half of the data more difficult. In 2003, the survey was improved by carefully decreasing the number of sites from 90 to the current 43 (Odom, 2003). The discontinuation of sites throughout the years has created a non-uniform database. The inconsistency of the stream survey data creates

problems during statistical analysis. Along with different sites for different years, the base flow/storm flow classification is also inconsistent. It starts in 1993 and ends in 2010, while data up to 2012 will be analyzed here.

1.3.2 Elevation Bands

Elevation, along with the stream system a site belongs to, are the most important characteristics of each site location. 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, NO_3^- , SO_4^{2-} , the base cations. Overall, results from the Biotics Effects report found that stream pH and ANC decreased at -.32 units and -35.73 eq L-1 respectively, per 1,000-ft elevation gain (Meijun Cai, 2013). 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. Because pH decreases with an increase of elevation, elevation bands are used to characterize elevation. Conductivity, chloride, and base cations were also found to significantly decrease with elevation gain. Sulfate showed no significant trend with elevation, however nitrate 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 1993-2010 with 2011. The data showed lines of similar slopes with different intercepts, which was interpreted to mean increasing pH at all elevations in GRSM streams. Acid deposition increases with elevation in the GRSM. Higher elevation experience increased sulfate and prolonged acidification if soil desorption becomes a dominant geochemical watershed process, which could occur if pH increased to 6.0 and sulfate dropped below 50 eq L-1 (UTK, 2012). From a management perspective, the Biotic Effects Report contains limitations in the analyses to assess long-term changes 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 sam- pling 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 concerns of Kenith Odom presented 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.

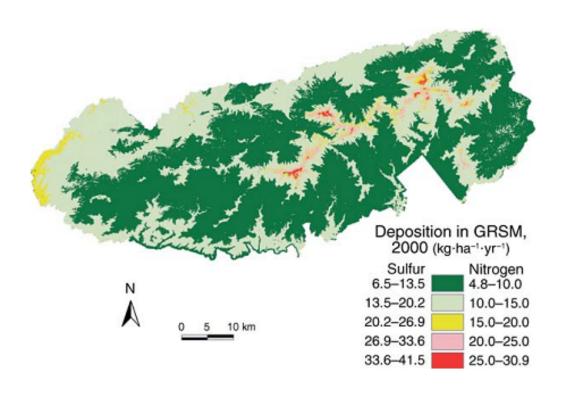


Figure 1.2: Modeled atmospheric deposition of N and S for the year 2000 and presented in Weathers et al. (2006).

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. As can be seen in Figure 1.2, 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 rethought to attempt to strengthen the higher elevations. A cluster analysis was explored for the task but it was not successful. There was too much variation to cluster by elevation only. A short report of the cluster analysis is presented in Appendix H. Because the cluster analysis was not successful, the elevation boundaries which divided the bands were moved to include more or less sites.

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	, , , , , , , , , , , , , , , , , , , ,
			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 Time sets

Time trends are a general way to assess the health of the streams in the GRSM. Instead of representing a single point in 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 (Meijun Cai, 2013). Though these papers analyzed similar years (Robinson:1993-2002, Cai: 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 Meijun Cai (2013), 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 Meijun Cai (2013) 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 power plants installed scrubbers onto their smoke stack exhaust. The hypothesis being the SO₄²⁻ concentrations will be noticeably different, and this difference could indicate a need for further study. 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 formatted for 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_3^- , 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). 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.

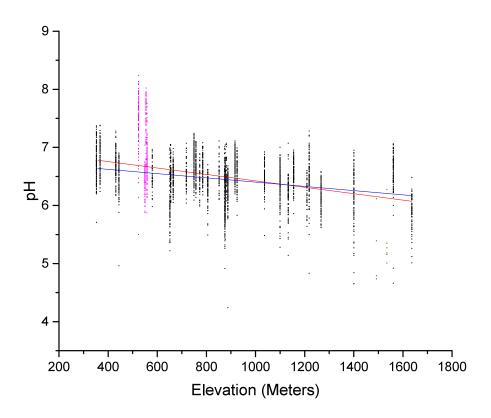


Figure 1.3: pH plotted vs. Elevation. With and without outliers.

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, which is important

to address for trend analysis (Helsel and Hirsch, 1992). Figure 1.3 shows the pH vs. elevation plot, which shows 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 represents the 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 1.3 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. 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, because the measurements are significantly different from the average. 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 Meijun Cai (2013). Unfortunately, the data analyzed for this paper goes through the year 2012, and water quality data after 2010 is not characterized for base flow/storm flow. If all storm flow observations are to be considered influential, the years 2011 and 2012 will need to be characterized. 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.

1.6 Objectives

Objectives of 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 (1000-2000ft, 2000-2500ft, 2500-3000ft, 3000-3500ft, 3500-4500ft, 4500j)?
 - Time trends
 - Means Comparisons
- Determine the statistical power for water quality parameters based on frequency and elevational location.
 - Post Hoc Analysis
 - A Priori Analysis

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 Stream Survey can by analyzed for trends through a trend analysis. It is used to determine the condition of the parks 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 Wildlife and Fisheries Deptartment in 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 (Meijun Cai, 2013). 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 (Meijun Cai, 2013). The trend analysis of Robinson et al. (2008) used data from the 90 site survey while the trend analysis in Meijun Cai (2013) used only 43. The difference in survey sites may affect the trend analysis, and for this reason both time periods will be analyzed separately here 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 these.

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 with the data. A variable with an 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)	$(.415 \times \text{Sum Base Cations}) + (185 \times$	0.984	0.049
	SO_4) + (.595 × Conductivity) + (102 ×		
	NO_3)+(.019×Julian Date)+(.005×Cl)+		
	$(.005 \times \sin(\theta))$		
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		
	Julian Date) + $(.051 \times Cl)$ + $(.047 \times Cl)$		
	$\sin(\theta)) + (.031 \times \cos(\theta))$		
SO_4 (3116)	$(166 \times NO_3) + (2.318 \times Conductivity) +$	0.720	< 0.001
	$(-3.229 \times ANC) + (1.033 \times$		
	Sum Base Cations) $+ (.042 \times \text{Julian Date})$		

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 is due to T or X. 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. Table 2.2 can be used as a summary of the step-wise proceses.

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.

		Dependents for step-wise 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 Appendix C.1 and the equations calculated using the three time variables only are recorded in Appendix C.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 in Appendix C.1 are insignificant, while 50 of the 72 trend lines in Appendix C.2. are insignificant. Insignificance is caused by a regression line with a p-value greater than the chosen α of .05. When this happens the hypothesis that β (the coefficient) \neq 0 is rejected. Meaning that there is greater than a 5% chance that $\beta = 0$ or in this case the Julian date coefficient =0.

2.2.1 Step-wise Julian date coefficients

pH

pH time trends in Appendix C.1 were negative for only three statistically significant regression lines, all in the time range of 1993-2002, in elevation classes 2, 3, and 5. There is one insignificant negative trend in the third time set (2009-2012) and 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 set 2 have a smaller slope in set 3, and one of the negative trends in set 2 becomes positive in set 3. When comparing time set 2 to set 3, ANC trends are growing over time.

Nitrate

The trends for NO_3^- in in time set 1 are half positive and half negative. The trends in time set 2 are all positive, but there is a decreasing trend in time set 3, elevation class 4.

Sulfate

 SO_4^{2-} contains mixed positive and negative trends for time set 1 but all positive trends for set 2. Half of the SO_4^{2-} trends in time set 3 are negative in elevation bands 1, 3, and 6.

2.2.2 Julian date coefficients from time variables only

In Appendix C.2 only 20 of the 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 has zero significant lines, time sets 2 and 3 combined are 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 in Appendix C.1.

ANC

There are only two significant regression lines in for ANC in Appendix C.2. Elevation class 5 in time set 1 has a decreasing trend of -.148, and while there are no significant lines in time set 2, time set 3 elevation class 5 has a positive trend of .891.

Nitrate and Sulfate

 NO_3^- and SO_4^{2-} both had negative trends in time set 1 class 1. These are the only significant decreasing trends exhibited for either NO_3^- or SO_4^{2-} in Appendix C.2. But both have positive trends in set 2 at elevation classes 1, 2, 4 and 6. Neither variable have significant lines in set 3.

2.2.3 Elevation trends

Table 2.3: 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 2.3 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 Appendix C.1 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 different trends seen in the old elevation classes from Robinson et al. (2008) of 1, 2, and 3 and elevation class 1 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 set 1 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 is what 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 set 1 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 Meijun Cai (2013) reports a decrease for pH and ANC of -0.32 pH units and -35.73 μ eq L⁻¹ per 1000-ft elevation gain or 302-m elevation gain respectively. Multiply these results by 3.3 to convert to meters and pH and ANC are -1.056 pH units and -117.909 μ eq L⁻¹ per 1000-m elevation gain respectively. A comparison between these results and those reported in Table 2.3, In time set 3, both pH and ANC are significantly lower with trends of -.0286 pH units and -35.689 μ eq L⁻¹ per 1000-m increase respectively. The differing amounts of time and number of sites in each study could account for these differences.

Nitrate and Sulfate The positive SO_4^{2-} trends seem to decrease by 2 μ eq L⁻¹ between set 1 and set 2 in Table 2.3 and then by 6 μ eq L⁻¹ between set 2 and 3. In contrast, a negative insignificant elevational trend was found in Meijun Cai (2013) for the years 1993 to 2009. NO_3^- follows a similar pattern as SO_4^{2-} 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 μ eq L⁻¹ between set 1 and set 2 and then by almost 5 μ eq L⁻¹ between set 2 and set 3.

2.3 Discussion and Conclusions

It is interesting 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 1.3 clearly shows a decreasing trend for pH while increasing the elevation. Increasing acidification with increased elevation was observed in Meijun Cai (2013) 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 of Appendix C.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 agrees with Meijun Cai (2013) 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 high elevation site Noland begin to drop along with emissions from Kingston and Bull run power plants.

Water quality is increasing. pH and ANC are rising and the 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 Meijun Cai (2013). 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 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

Means Comparison

3.1 Methods

3.1.1 Introduction

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

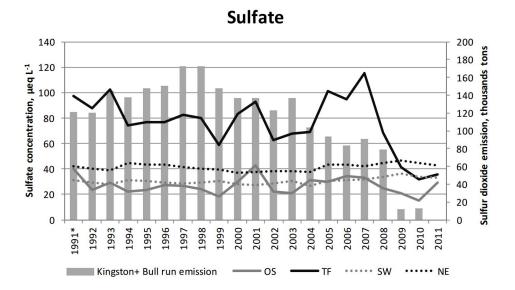


Figure 3.1: Yearly sulfur dioxide emissions for Kingston and Bull run, with yearly Noland Divide high elevation site sulfate concentrations. Figure borrowed from Meijun Cai (2013).

Interestingly the through fall SO₄ concentrations dramatically decline from about 115 μ eq L⁻¹ in 2007 to about 30 μ eq L⁻¹ in 2010. A reduction in sulfur dioxide emissions could correlate to a reduction in SO₄ concentrations measured in 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 Stream Survey can give a fuller representation of the affects of air pollution from local power plants. So 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 vector 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. 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, NO₃, and SO₄). Each group compared is the same data groups from the stream survey data analyzed in chapter 2 and chapter 4.

Table 3.1: Bonferroni comparisons between multiple groups

Elevation Classes	рН		ANC		Nitrate			Sulfate				
	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	$\overline{\neq}$	\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	=	=	=	=	=	=	=	=	=

3.2 Results

The group means comparisons are represented by equal signs and unequal signs and are taken from the 95% C.I. determined in the study. 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. They are presented in Appendix D.1.

The set comparisons for pH are the first comparisons presented, they include more unequal sets than any other water quality variable. Much of the comparisons are unequal except between elevation class 2 which are all equal and class 4 and 6 which show are equal in 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 and the smallest in elevation class 6. Unfortunately elevation class 2 always contains the lowest means instead of Elevation class 6. And elevation class 3 behaves as if it should be between elevation class 5 and 6.

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

NO₃ elevation classes 4 and 6 are 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, which is all time sets being unequal with time set 3, showing all being equal except for sets 1 and 2. In elevation class 2 sets 3 and 2 are equal and in elevation class 5 sets 3 and 1 are equal. The line graphs for the odd numbered elevation classes of NO₃ all have decreased mean values from set 2 to 3. In elevation classes, 2 and 4 the mean values for set 3 are higher than those in set 2 but the difference of the means over times is decreasing. Overall the NO₃ figures show mostly decreasing concentrations over time, except for class 6 which is always increasing. The odd classes all have decreasing negative trends from set 2 to set 3 while classes 2 and 4 have decreasing positive trends between set 2 and 3.

SO₄ points to all three time sets being equal across all elevation classes except for class 2, which shows equality for 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 SO₄ 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 SO₄ are larger than their respective set 2 means except for those in class 2 which throughout has negative trends.

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 SO₄. Other outcomes were also unexpected such as the increase in pH over time and the abnormal ANC concentrations. The apparent decrease in ANC overtime as indicated in the Bonferroni figures was unexpected both because this is in contrast to the Julian date coefficients for ANC and pH has an increasing trend overtime. Because the Bonferroni method calculates significant means for the water quality vector the difference between the figures and the trends suggests 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 SO₄ 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 SO₄ results. A significant negative difference in means for set 3 compared to sets 1 and 2 would support the hypothesis. The inequalities present between the 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 sets are unfortunately mostly equal. This suggests a bank of SO_4 where previous SO_4 pollution is collected and a steady concentration is being released into the steams which are being measured with grab samples. In this way until that bank is depleted a significant difference in means may not be found.

Chapter 4

Power Analysis

4.1 Methods

4.1.1 Introduction

The 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. The trend analysis preformed in chapter 2 is a hypothesis test which comes with an inherent amount of error. It 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 β and can be seen in Table 4.1. β 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 β 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: Hypothosis test results (Helsel and Hirsch, 1992)

		Unknown True Situation					
		H_0 is true	H ₀ is false				
	Fail to	Correct decision	Type II error				
ion	reject H_0 Prob(correct decision) = $1-\alpha$		$ Prob(Type II error) = \beta $				
Decision	Reject H ₀	Type I error $Prob (Type I error) = \alpha$	Correct decision 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 post hoc and a priori analysis for many different statistical tests (Faul et al., 2009) Analysis can be run on many different hypothesis tests, power analysis for regression was used here. All 144 trend lines from chapter 2 were evaluated using a post hoc analysis and a priori analysis was used to project the current 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 of the already 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 required to achieve it.

A post hoc analysis was preformed for both of the Julian date coefficient tables from chapter 2, and are presented in Appendix E.1 and Appendix E.2. 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 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. ES is the only information that needs to be calculated before the analysis can be completed; the other inputs come from the trend analysis. 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 presented in Appendix E.1 and Appendix E.2. The ES calculation is completed by G*power after inputting the correlation coefficient (adj. r^2).

Post hoc

G*power uses ES along with the α (.05) used for the regression model, the number observations, and number of predictors in the model to output the power of the F test. 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; ES is described by Cohen as the probability to find a significant result (Cohen, 1992a). 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 from chapter 2.

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 α (.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 α .

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 trend analyses are reported in Appendix E.1 and Appendix E.2. They are broken into the four water quality variables (pH, ANC, NO₃, SO₄) and divided into the tree time sets (93-02, 03-08, 09-12), and then further divided into the six elevation classes. Each 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 in Appendix E.1 only eight of them were less than 1.00. And only two of the trend lines in Appendix

E.1 were insignificant. One of the insignificant trends was the trend for Nitrate, set 3, class 5, and along with insignificance the adjusted r^2 was negative and therefore the power could not be found. The other insignificant trend was pH, set 3, class 5, which also received the lowest observed power of .28. In large dissimilarity from the step-wise trend models, 52 of the 72 trends from Appendix E.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.

4.2.2 A priori

Power graphs

The traditional presentation for an a priori power analysis is the power graph. Here the powers are 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 NO₃, which are the same because they contain the same number of predictors from the 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 adequate powers, SO₄ needs almost 30 samples than the time model to reach a power of .80 with an ES of .15. The power graphs for pH, ANC and NO₃, SO₄, and Time are plotted in Appendix F respectively. And Table 4.2 was created for easier comparison.

Table 4.2: Sample sizes at a power of .80

ES	0.15	0.35
рН	97	45
ANC and NO3	98	51
SO4	103	48
Time	76	35

This table shows the sample size values for both ES curves at a power of .80. Again all are similar except for the time graph, which has at least half as many predictors in its time trend equation as the others.

A priori manipulation

Table 4.3: 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

The results of the a priori analysis are presented in Table 4.3 but are inconvenient and require manipulation in order to apply them to the 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 4.3 to have a powerful trend analysis. But adding sites is cheaper and can solve the poor elevational distribution of the sites in the Stream Survey.

The a priori power analysis can be manipulated to calculate a number of sites per elevation band for the 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 4.3 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 4.3. 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 NO₃. For the step-wise equations N will be rounded up to 110 and labeled N_b .

Table 4.4: Samples/year to achieve a power .80 (N_b)

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

These are presented in Table 4.4, which has been calculated out to four years. So that 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.

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

Table 4.5: Years to achieve a power of .80

Elevation Bands	Site #	Current n/yr	рН	ANC NO_3	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
	483, 147, 148, 484					
3	114, 481, 482, 149,	62	1.58	1.76	1.66	1.24
	66, 492, 137, 293, 270,					
	493, 485, 144, 224					
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

This scenario was followed through with both methods of trend lines. Table 4.5 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 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 NO₃ 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 4.6: 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

Table 4.7: 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

Tables Table 4.6 and Table 4.7 correspond to the two trend models: step-wise and time. 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 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 4.6 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

4.3.1 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, Table 4.3, it can easily be recognized that as the number of observations in Appendix E.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 r² it declines as the r² does, the higher the r² the better. But for a calculated ES of .15 the adjusted r² doesn't need to be very high. So as the analyzed trend line for pH in time set 3 elevation class 5 has an adjusted r² 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 post hoc analyses cannot be the number of observations because the number of observations used in Appendix E.1 are the same as those Appendix E.2. The differences are between the adjusted r^2 values, which are very low for Appendix E.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 in Appendix E.1 are not terrible. Of the 20 significant lines eleven have a power equal to or above .80.

4.3.2 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 step-wise 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 then the a priori analysis in not 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 4.6, 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 two and six from class three. One site each need to be added to classes five and six and three should be added to class six. There are too

many sites in the lower elevation classes of two and three and not enough sites in the higher elevation classes of four, five, and six. 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
2003-2008	3	762-914.4 (2500-3000)	299	-26.45	1591.06	172.82
003	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
	1	304.8-609.6 (1000-2000)	325	12.32	85.01	36.09
02	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
1:0	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
-20	3	762-914.4 (2500-3000)	308	10.44	490.01	54.25
2003-2008	4	914.4-1066.8 (3000-3500)	123	13.88	61.31	29.04
30	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
-20	3	$762-914.4 \ (2500-3000)$	228	13.59	317.63	58.15
2009-2012	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

Appendix C

Julian Date Coefficients

C.1 Step-wise Method

C.1.1 Set 1: 1993-2002

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

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

C.1.2 Set 2: 2003-2008

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

Elevation class	Elevation range m (ft)	Number of sites	Julian date coefficient, μ eq/L or pH units (model adjusted r^2) (p-value)			
010000			рН	ANC	Nitrate	Sulfate
1	304.8-609.6 (1000-2000)	5	0.150 0.781	-0.004 0.996	0.038 0.551	0.039 0.673
			0.000	0.000	0.000	0.000
2	609.6-762 (2000-2500)	9	0.275	0.033	0.044	0.044
2			0.348 0.000	0.779 0.000	0.816 0.000	0.893 0.000
3	762-914.4	13	$0.156 \\ 0.663$	$0.005 \\ 0.996$	$0.072 \\ 0.637$	$0.034 \\ 0.923$
	(2500-3000)		0.000	0.000	0.000	0.000
	914.4-1066.8	4	0.249	-0.028	0.092	0.110
4	(3500-3500)		0.400	0.779	0.405	0.343
			0.000	0.000	0.000	0.000
	1066.8-1371.6 (3500-4500)		0.137	-0.020	0.204	0.135
5		4	0.300	0.739	0.562	0.884
			0.027	0.000	0.001	0.000
	1371.6 < (4500 <)		0.359	0.127	0.074	0.161
6		2	0.317	0.812	0.832	0.844
			0.000	0.000	0.000	0.000

C.1.3 Set 3: 2009-2012

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

Elevation class	Elevation range m (ft)	Number of sites _	Julian date coefficient, μ eq/L or pH units (model adjusted r^2) (p-value)			
Class	runge in (10)	51005	рН	ANC	Nitrate	Sulfate
1	304.8-609.6 (1000-2000)	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 (2500-3000)	13	0.056	0.007	0.019	0.050
3			0.766	0.997	0.598	0.915
			0.000	0.000	0.000	0.000
	914.4-1066.8		0.413	-0.006	-0.013	-0.068
4	(3500-3500)	4	0.593	0.772	0.635	0.529
	(9900 9900)		0.000	0.000	0.000	0.000
	1066.8-1371.6		-0.115	0.901	0.098	0.015
5	(3500-4500)	4	0.158	0.540	-0.272	0.658
	(9900 4900)		0.130	0.001	0.975	0.000
	1371.6<		0.289	0.059	0.097	-0.059
6	(4500 <)	2	0.286	0.809	0.881	0.861
	(4000 <)		0.000	0.000	0.000	0.000

C.2 Temporal Variables

C.2.1 Set 1: 1993-2002

Table C.4: Julian date coefficients from the time variable equations for set 1.

Elevation class	Elevation range m (ft)	Number of sites	Julian date coefficient, μ 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	$0.054 \\ 0.047 \\ 0.321$	0.089 0.024 0.106	-0.138 0.016 0.022	-0.190 0.045 0.001
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	-0.075 0.009 0.142
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 0.355
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	0.095 -0.016 0.313
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	0.092 -0.010 0.331
6	1371.6< (4500 <)	2	0.156 0.096 0.092	-0.016 0.075 0.863	-0.208 0.092 0.058	-0.036 -0.009 0.707

C.2.2 Set 2: 2003-2008

Table C.5: Julian date coefficients from the time variable equations for set .

Elevation class	Elevation range m (ft)	Number of sites	Julian date coefficient, μ eq/L or pH units (model adjusted r^2) (p-value)			
Class	range in (10)	BICES	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
	600 6 762	9	0.145	-0.090	0.178	0.138
2	609.6-762 (2000-2500)		0.061	0.081	0.043	0.014
			0.012	0.114	0.002	0.017
	762-914.4 (2500-3000)	13	0.103	-0.006	0.047	0.099
3			0.020	-0.003	-0.003	0.006
			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		0.135	-0.112	-0.176	0.067
5	(3500-4500)	4	-0.069	0.337	-0.082	-0.024
	(5000-4000)		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
	(1000 <)		0.041	0.274	0.020	0.002

C.2.3 Set 3: 2009-2012

Table C.6: Julian date coefficients from the time variable equations for set .

Elevation class	Elevation range m (ft)	Number of sites	Julian date coefficient, μ 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
	(1000-2000)		0.122	0.718	0.619	0.207
	609.6-762		0.141	0.017	0.020	-0.062
2	(2000-2500)	9	0.052	0.056	0.011	-0.010
			0.037	0.800	0.767	0.376
	762-914.4	13	-0.034	-0.027	-0.036	0.078
3	(2500-3000)		-0.009	-0.002	-0.004	-0.007
			0.611	0.684	0.592	0.246
	914.4-1066.8		0.405	0.032	-0.067	-0.129
4	(3500-3500)	4	0.200	0.161	-0.016	-0.011
	(9900 9900)		0.000	0.733	0.518	0.215
	1066.8-1371.6		-0.031	0.891	0.052	-0.414
5	(3500-4500)	4	0.218	0.466	-0.039	-0.076
	(3000-4000)		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
	(4000 <)		0.023	0.462	0.859	0.068

Appendix D

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D.1 pH

Figure D.1: pH set means, class 1

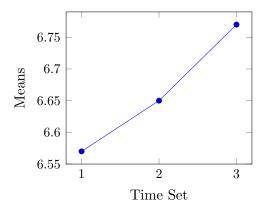


Figure D.3: pH set means, class 3

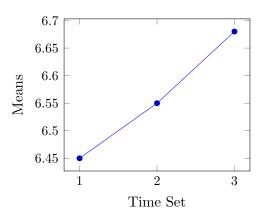


Figure D.5: pH set means, class 5

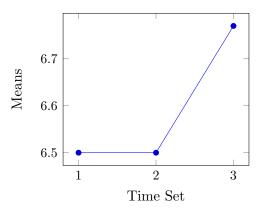


Figure D.2: pH set means, class 2

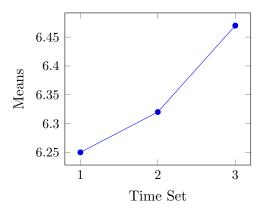


Figure D.4: pH set means, class 4

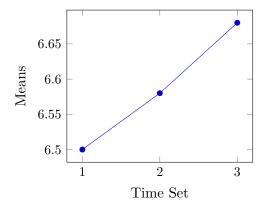
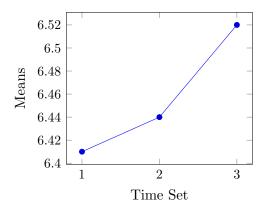


Figure D.6: pH set means, class 6



D.2 ANC

Figure D.7: ANC set means, class 1

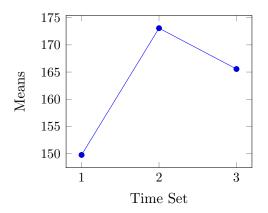


Figure D.9: ANC set means, class 3

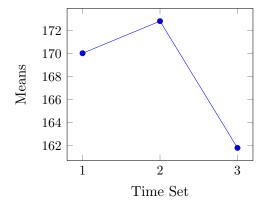


Figure D.11: ANC set means, class 5

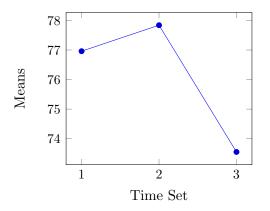


Figure D.8: ANC set means, class 2

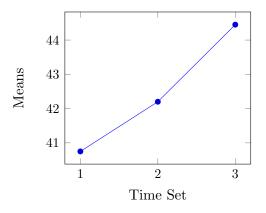


Figure D.10: ANC set means, class 4

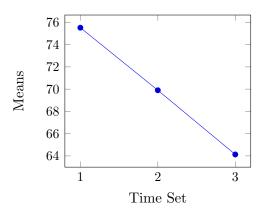
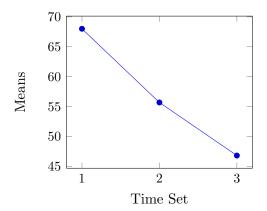


Figure D.12: ANC set means, class 6



D.3 Nitrate

Figure D.13: NO_3^- set means, class 1

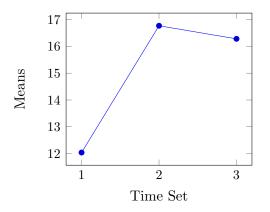


Figure D.15: NO_3^- set means, class 3

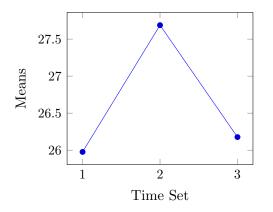


Figure D.17: NO_3^- set means, class 5

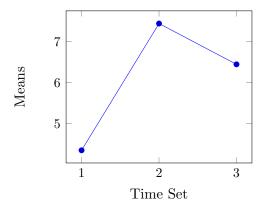


Figure D.14: NO_3^- set means, class 2

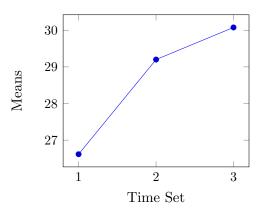


Figure D.16: NO_3^- set means, class 4

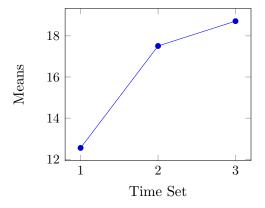
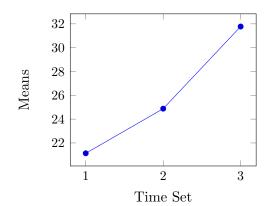


Figure D.18: NO_3^- set means, class 6



D.4 Sulfate

Figure D.19: SO_4^{2-} set means, class 1

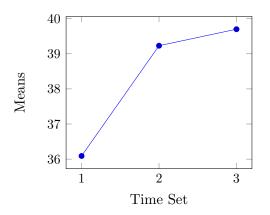


Figure D.21: SO_4^{2-} set means, class 3

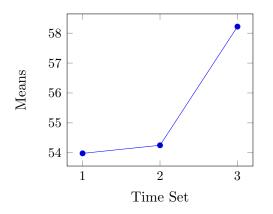


Figure D.23: SO_4^{2-} set means, class 5

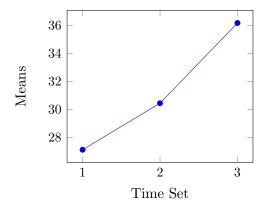


Figure D.20: SO_4^{2-} set means, class 2

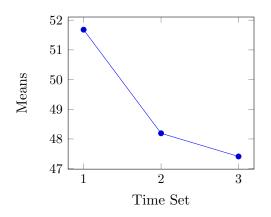


Figure D.22: SO_4^{2-} set means, class 4

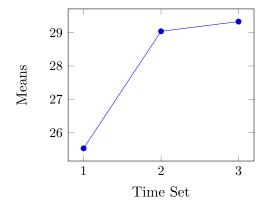
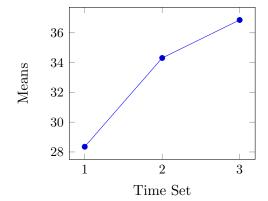


Figure D.24: SO_4^{2-} set means, class 6



Appendix E

Post Hoc Power Analsysis

E.1 Step-Wise Variables

Post hoc power analysis using G*power and a calculated ES, α is .05. **Bold** results are insignificant.

E.1.1 pH

Table E.1: 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
16	5	116	0.165	0.20	0.96
	6	110	0.505	1.02	1.00
	1	255	0.781	3.57	1.00
80	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

E.1.2 ANC

 ${\bf Table~E.2:}~{\rm ANC~Step\text{-}Wise~Post~Hoc~Power~Analysis~Results}$

Set	Class	N	Adjusted r^2	Effect Size	Actual Power
	1	327	0.985	65.67	1.00
0.5	2	392	0.603	1.52	1.00
1993-2002	3	398	0.971	33.48	1.00
993	4	120	0.709	2.44	1.00
13	5	116	0.760	3.17	1.00
	6	110	0.802	4.05	1.00
	1	255	0.996	249.00	1.00
08	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

E.1.3 NO3

 ${\bf Table~E.3:~Nitrate~Step-Wise~Post~Hoc~Power~Analysis~Results}$

Set	Class	N	Adjusted r ²	Effect Size	Actual Power
	1	275	0.503	1.01	1.00
0.5	2	377	0.699	2.32	1.00
1993-2002	3	365	0.359	0.56	1.00
993	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

E.1.4 SO4

 Table E.4: Sulfate Step-Wise Post Hoc Power Analysis Results

Set	Class	N	Adjusted r ²	Effect Size	Actual Power
set	Class	11	Adjusted 1	Effect Size	Actual Fower
	1	325	0.569	1.32	1.00
00	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
13	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

E.2 Temperol variables

Post hoc power analysis using G*power a calculated ES, an alpha of .05 with the variables: $\sin(\theta)$, $\cos(\theta)$, and Julian date only. **Bold** results are insignificant.

E.2.1 pH

 ${\bf Table~E.5:~pH~Time~Variable~Post~Hoc~Power~Analysis~Results}$

Set	Class	N	Adjusted r ²	Effect Size	Actual Power
	1	327	0.047	0.049	0.93
01					
300	2	393	0.128	0.15	1.00
-2(3	400	0.013	0.01	0.46
1993-2002	4	121	0.059	0.06	0.61
10	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

E.2.2 ANC

 Table E.6: ANC Time Variable Post Hoc Power Analysis Results

	<u></u>	N.T.	A 1: 1 2	Da + a:	A , 1 D
Set	Class	N	Adjusted r ²	Effect Size	Actual Power
	1	327	0.024	0.02	0.65
00	2	392	0.189	0.23	1.00
1993-2002	3	398	0.000	0.00	0.06
993	4	120	0.294	0.42	1.00
13	5	116	0.381	0.62	1.00
	6	110	0.075	0.08	0.69
	1	255	0.001	0.00	0.07
08	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

E.2.3 NO3

 ${\bf Table~E.7:~Nitrate~Time~Variable~Post~Hoc~Power~Analysis~Results}$

Set	Class	N	Adjusted r ²	Effect Size	Actual Power
	1	275	0.016	0.02	0.39
02	2	377	0.017	0.02	0.55
-20	3	365	-0.004	NA	NA
1993-2002	4	105	-0.027	NA	NA
15	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

E.2.4 SO4

 ${\bf Table~E.8:}~{\bf Sulfate~Time~Variable~Post~Hoc~Power~Analysis~Results}$

Set	Class	N	Adjusted r^2	Effect Size	Actual Power
	1	325	0.045	0.05	0.92
0.5	2	390	0.009	0.01	0.32
-20	3	391	-0.004	NA	NA
1993-2002	4	119	-0.016	NA	NA
13	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

Appendix F

A priori analysis power graphs

F.1 pH

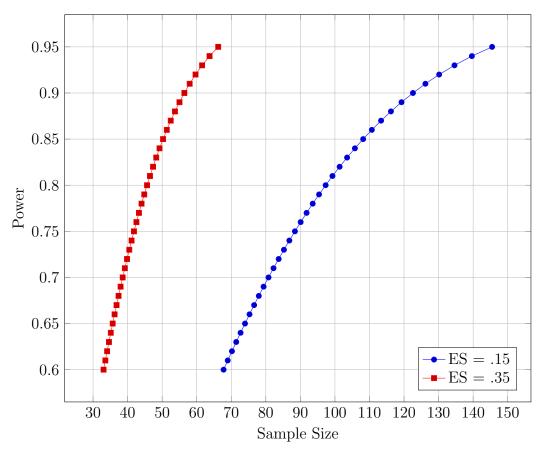
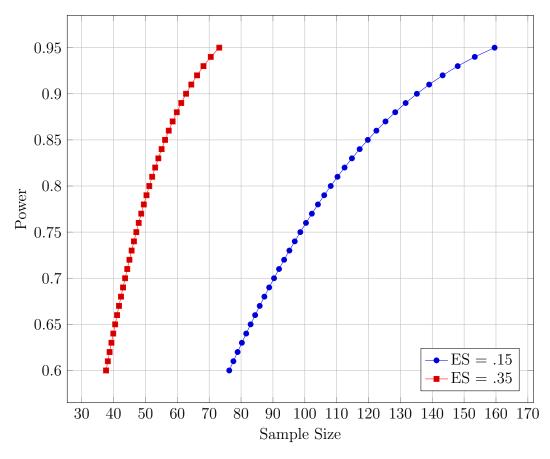


Figure F.1: A priori pH power graph

F.2 ANC and Nitrate

Figure F.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.



F.3 Sulfate

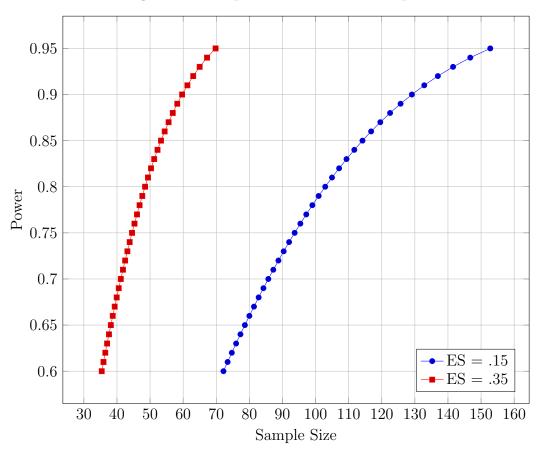


Figure F.3: A priori Sulfate Power Graph

F.4 Time Variables

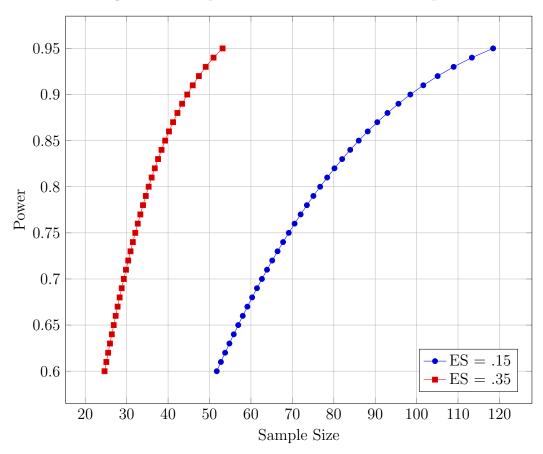


Figure F.4: A prioir Time Variables Power Graph

Appendix G

Cluster Analysis

G.1 Infuential Observations

Cluster analysis performed by Tim Pobst and David Mercer. David Mercer is a student employee of OIT, he helps with statistics.

The excel file used is called Complete 387 stream chemistry 1993 to 2012. The data sheet used is labeled dataset. Furthermore in order to identify trends only the years 2005 to 2012 were used. This is because the frequency of sampling needs to be constant in order to detect trends, which is used in finding outliers. The years of 2005 to 2012 mark the period for the current stream survey network and is also the largest data set with a constant frequency. It includes the six watersheds I was asked to evaluate plus Hazel creek watershed.

Wards minimum variance method is affected by outliers. The first data analysis performed was to find the outliers in the data. Figures were created of pH vs. Month, Elevation class, Elevation (m). These are shown in figures 1 through 3. Figure 1 is pH vs. Month; this was figured to look for seasonality and closely resembles the figure of pH vs. Time. As can be seen in figure 1, there are many outliers, which are the data points above and below the boxplots. An outlier is more than two quartile lengths away from the mean. Figure 2 is pH vs. Elevation class which was graphed in order

to see a trend in pH and elevation. In this figure class 3 and 9 have very large pH ranges which occur in just 500 ft. of elevation. The reasons for these large ranges will be shown in pH vs. watershed and site ID. Figure 2 also includes many low outliers in elevation classes 5 and 6, in fact, Figure 3 was created in order to see what was making elevation classes 3 and 9 so large. The high pH values in elevation class 3 and to some extent 4 can be accounted for as part of Abrams watershed. Abrams watershed is underlain by cades sandstone and has high natural ANC to buffer any added acids. The whole Abrams watershed will be taken out as an outlier. There many low data points in the range of elevation class 9. These points are well grouped and are sites with consistently low pH values. They turn out to be sites 252 and 237 which are affected by road cuts into an Anakeesta formation which is high in sulfur and lowers the pH drastically. These sites have means that are so low that they will be taken out as to influential. Also noticeable are many low outliers, many of these can be attributed to storm flow. Storm flow periodically lowers pH as storms increase Nitrates and Sulfates in the stream. Storm flow is a column in the data and is characterized as the top 5% of stream flows. Storm flow is also removed as an outlier. Figure 4 shows pH vs. Site ID without any of the previously stated influential observations. Many of the lower outliers can be explained by storm flow conditions. Figure 4 is the final figure concerning outliers. Abrams watershed, storm flow, and sites 237 and 252 have all been taken out. There are three sites left with low means. Sites 4 and 137 are both from Cosby and Cosby only has 4 sites. All three of the means of these sites are within the outer quartiles of other sites; therefore they are not outliers in themselves.

Here we have some summary statistics taken while removing the outliers. The drop in count is due mainly to storm flow. The mean does not change drastically from all outliers being present to removing all outliers. The standard deviation does drop two tenths from everything included to all outliers taken out. Of course, the max is dropped when Abrams is taken out, and the minimum is raised when storm

Table G.1: Used for detection of influential observations

Summary Section of pH (Including Abrams)						
Count 1397	Mean 6.485132	Standard Deviation 0.6049951	Standard Error 0.01618653	Minimum 4.215162	Maximum 8.099278	Range 3.8841
Summary Section of pH (Excluding Abrams)						
Count 1239	Mean 6.403315	Standard Deviation 0.5529732	Standard Error 0.01570972	Minimum 4.215162	Maximum 7.370326	Range 3.1552
Summary Section of pH (Excluding Abrams and storm flow and sites 237 and 252)						
Count 614	Mean 6.511126	Standard Deviation 0.3904229	Standard Error 0.01575619	Minimum 4.659964	Maximum 7.370326	Range 2.7104

flow and sites 237 and 252 are removed, shrinking the range by a full pH point. These are all signs that we are successfully removing outliers.

The next couple of figures (figures 5 through 7) are the similar to the earlier figures except they do not have any outliers. The most important figure is Figure 5 because it is pH vs. Elevation class. If we want to run a cluster analysis to get new elevation classes by pH then we hope to see this figure show a clear, well defined trend. But we don't ,elevation class 3 and 10 have much lower means than the rest of the elevation classes. Class 3 includes Cosby watershed which may account for its being so low, specifically site #4. Class 10 is low because of site #234 from Road prong. And then there are a couple of low outliers in the upper elevation classes. If the outliers could not be explained then they were not excluded.

G.2 methods

Wards minimum variance is a distance method by which clusters are created in order that the total variance of the data is minimized. It begins with every data point as its own cluster and then combines the two clusters that will create the least amount of change in the total variance. This is done until there is only one cluster left. At this point, the dendrogram is evaluated to choose how many clusters are best. This is

usually done by looking at the distance, or in Wards case amount of variation added, between the clusters. Large jumps in distance usually indicate natural clusters.

The goal for this cluster analysis is to create elevation bands. A correlation matrix was created in JMP in order to see which variables correlated well enough with elevation to create clusters. The variables chosen were pH, ANC, Nitrate, and Sulfate. The first analysis identified two more site outliers; these sites were placed into clusters all on their own. Sites #251 in Oconaluftee is put into a cluster almost by itself at all numbers of clusters. This could mean that it is an outlier. After this site was removed site, #253 would be placed in a cluster all on its own. Both of these sites are affected by anakeesta rock formations, and are near site #252 was taken out early as an outlier.

After these, no more obvious outliers were found. A five cluster and a fifteen cluster grouping was chosen because they looked most natural. You can see this in the dendrogram by the long lines made before a cluster is joined, and they are the largest jumps in the clustering history.

G.3 Results

The results are summarized with distribution analysis from JMP. They are the distribution of pH, Stream System, and elevation within each proposed cluster. The first distribution is the pH distribution, it is the closest to normal. Another useful distribution which I did not show here is which sites belong to which clusters. These do not help much with elevation and pH but it may help determine why certain clusters formed.

G.3.1 5 Clusters

Cluster 1 is 68% West Prong Little Pidgeon which is known as the Road stream system. It includes 95 observations and the elevation ranges from 800 to 1700 meters. This is the smallest cluster and the one with the largest elevation range.

Cluster 2 is dominated by the Cosby stream system at 53% while including all of the other stream systems. Because it is dominated by Cosby which has only four sites that are fairly close together, the elevation is very tightly packed compared to the other clusters.

Cluster 3 is mostly West Prong Little Pidgeon and Cataloochee. It includes 215 observations and ranges from 1000 meters to 1600 meters in elevation. It includes the largest outliers of all the clusters.

Cluster 4 includes all road stream system sites. It has 149 observations and the elevations are split around 360 meters and 440 meters.

Cluster 5 is 59% Cataloochee. It has 307 observations but despite being the largest cluster its elevation ranges only 300 meters.

G.3.2 15 Clusters

The output for the 15 cluster distributions from JMP gave me a lot of trouble. Some of the outputs are cut off at the top that includes the titles but I assure you all of the distributions are in order.

I included the 15 cluster grouping just for some variety, but the way that hierarchical clustering works the 15 clusters will be just like the 5 clusters but divided smaller. Some of the clusters, clustered around a small number of sites and stream systems but overall the elevation is all over the place.

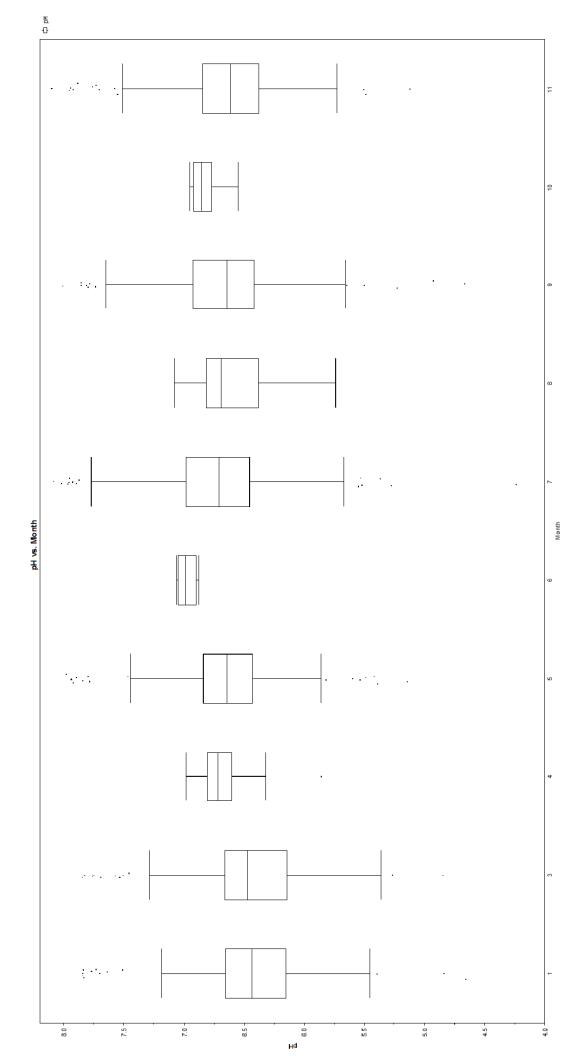
G.4 Discussion

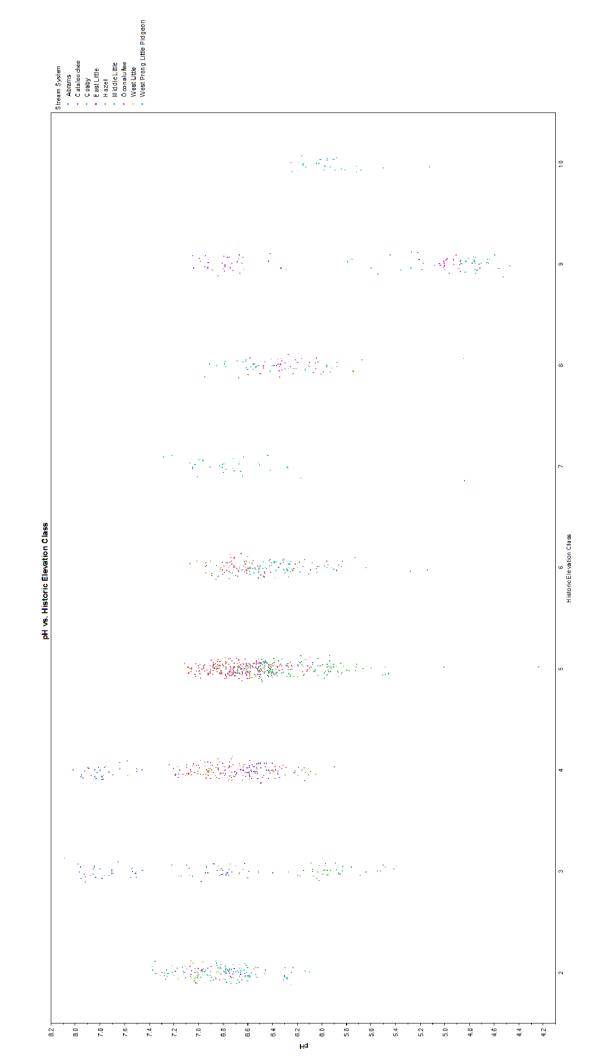
This cluster analysis does not show easy breaks between elevation or stream systems. There is too much variation in the data that is not explained by elevation. Natural elevation bands would be easier within individual watersheds.

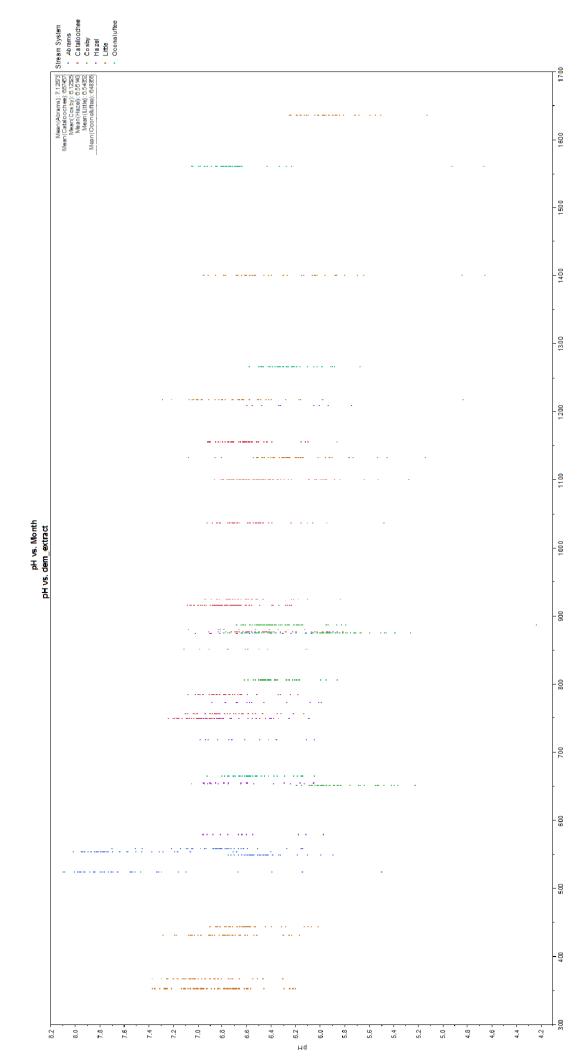
It would be better to run a cluster analysis with single site observations instead of multiple observations per site. However it is difficult to think of a single pH observation value that can represent all the changes pH may go through for a single site. Sites belong to multiple clusters because sites may act differently throughout time, and the pH may behave differently but the elevation is always the same.

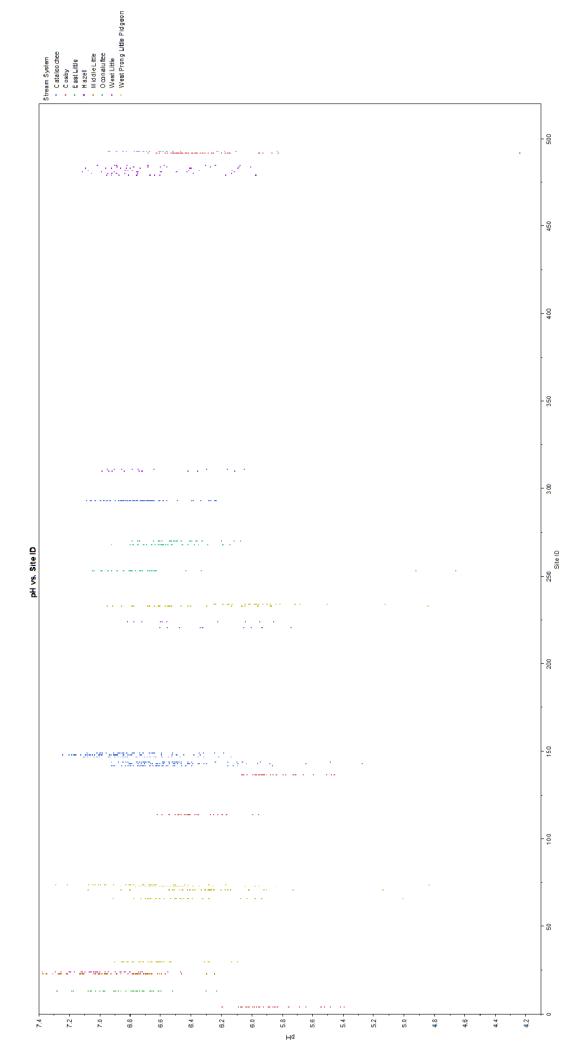
G.5 Figures

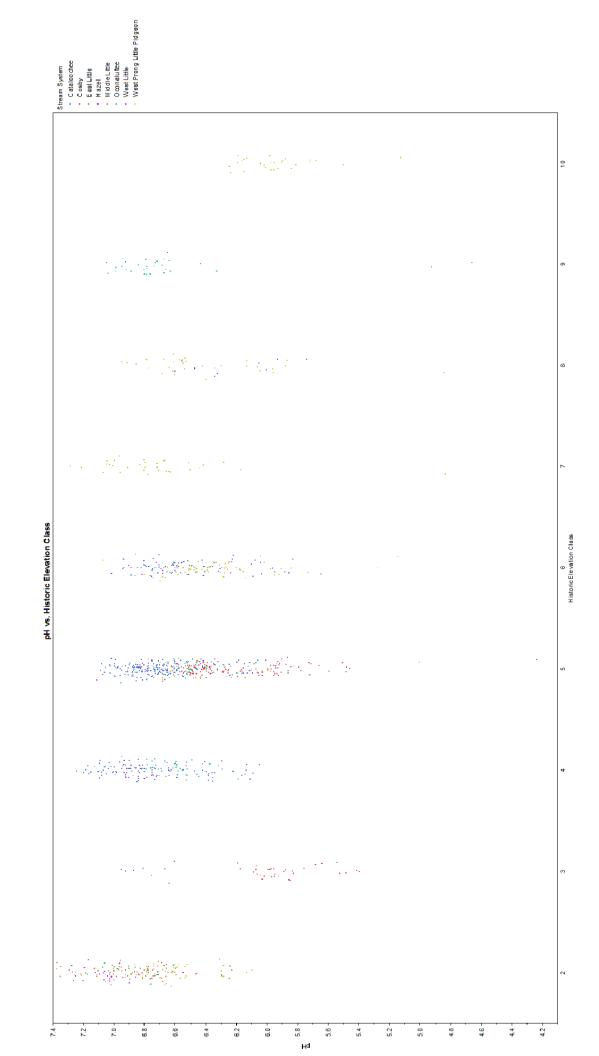
Figures were created in JMP, which means they look awesome in JMP, but they are less than perfect when you take them out of JMP. They could probably be remade better in Origin. The type is very small. If copies of the CAGraph#.pdf pdfs stay in the folder labeled figures then you can click the graph and it will open up the single file of the pdf.

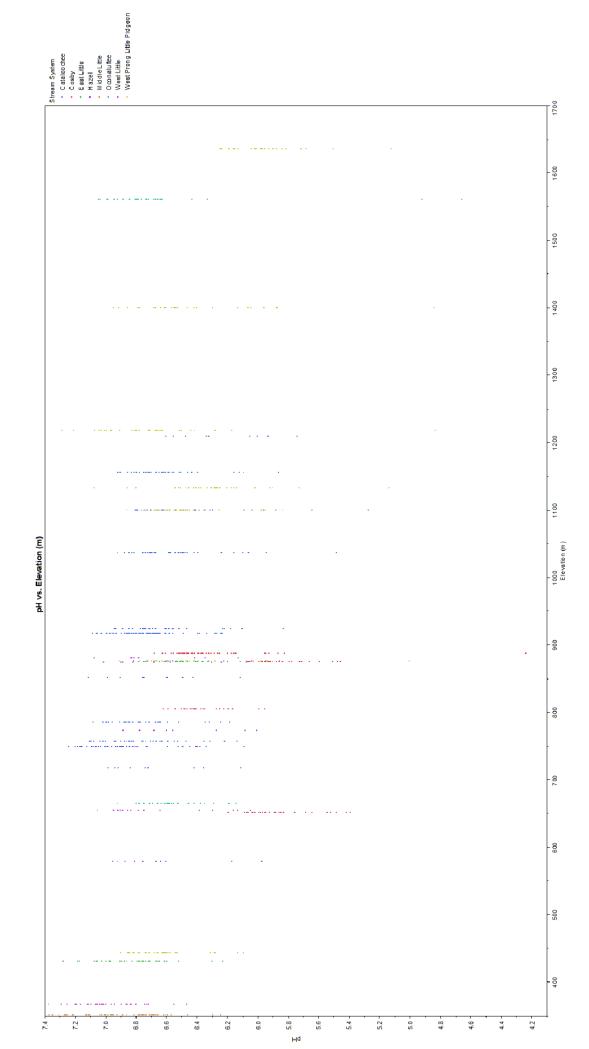


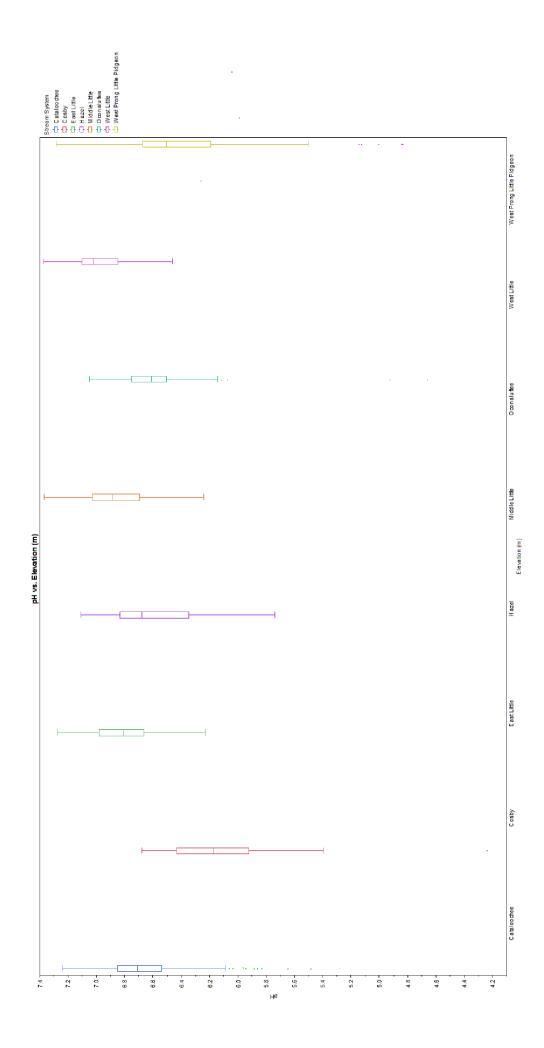












Vita

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.