To the Graduate Council:

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.

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(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

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Abstract

Abstract text goes here...

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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, over 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 US and its conservation is a high priority for the National Park Services (NPS) who are tasked with looking after 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 thing in the park which rely 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 contributers of manmade pollution to acid deposition is fossil fuel compustion 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) through smoke stacks high into the atmosphere where they react and fall to the earth as acid deposition. Once the pollutants have entered the environment they react with hydroxide, oxygen, water 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 interact with it, including the soils, and life forms as well as streams. The rate of stream acidification can be slowed by the alkalinity of the water which 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 thrugh leaching which is also caussed 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). And a constant removal of base cations can lead to chronic acidification by permantley 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 nearly 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 to 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 multiple 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 actually 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^-,SO_4^{2-},NO_3^-, ammonia (NH_4^+)), the base cations (Ca^{2+}, Mg^{2+}, K^+, Na^+), and dissolved metals (Al, Cu, Fe, Mn, Si and Zn). A ManTech^{TM} autotitrator was used for pH, ANC, and conductivity. A Dionex^{TM} ion chromatograph (IC) was used for the analysis of CL^-, SO_4^{2-}, NO_3^-, and NH_4^+. A Thermo-Scientific^{TM} Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) was used for the study of Ca^{2+}, Mg^{2+}, 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, location, pH, and constituent concentrations are aggregated in spread sheets and formated 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 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.

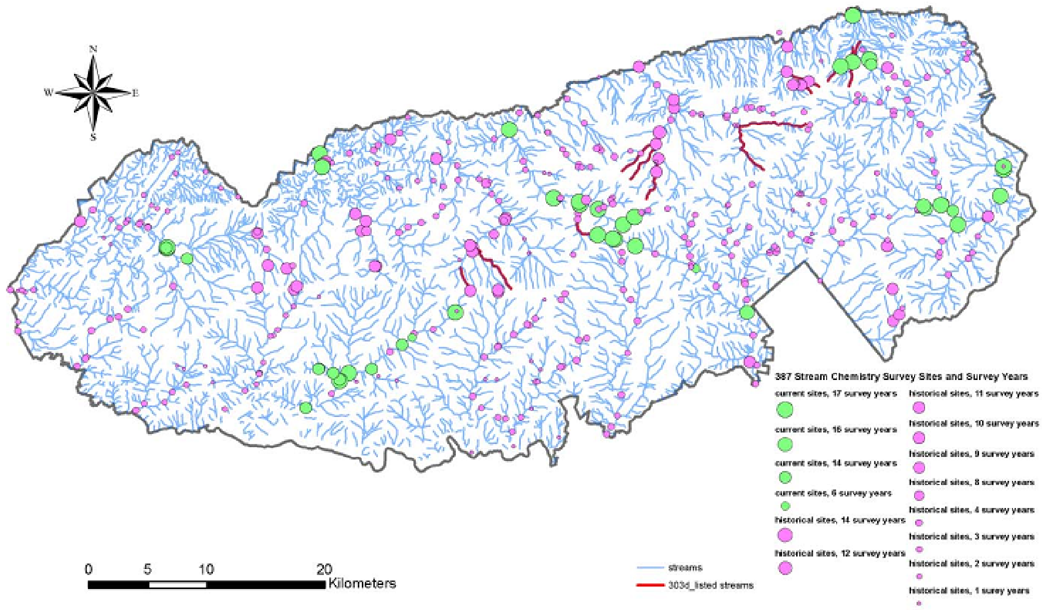

Figure 1.1: Site locations for the Stream Survey. This map takes into account the years 1993 to 2009 so 3 more years need to be added to the current sites.

The database is dynamic and changes along with the stream survey, theory, and lab methods and tools. Currently the collection, analysis, and formating 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 formating 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 harder. 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 over the years has created an non-uniform database. The inconsistency of the stream survey data can create problems during statistical analysis. Along with different sites for different years the baseflow/stormflow classification is also inconsistent which starts in 1993 and ends in 2010, while data up to 2012 will be analyzed here.

1.3.2 Elevation Bands

Besides which stream sysytema site belongs to the most important site location characteristic is elevation. 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 a greater amount. And 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 and the higher elevation streams would 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 sampling sites
1	<304.8 (<1000)	0	
2	304.8-457.2 (1000-1500)	4	
3	457.2-609.6 (1500-2000)	4	67.4
4	609.6-762 (2000-2500)	9	
5	762-914.4 (2500-3000)	12	
6	914.4-1066.8 (3000-3500)	6	16.3
7	1066.8-1219.2 (3500-4000)	1	
8	1219.2-1371.6 (4000-4500)	3	14.0
9	1371.6-1524 (4500-5000)	3	
10	>1524 (>5000)	1	2.3

Table 1.2: Historical elevation bands for the 43 site survey

Table 1.1 represents the 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 is not much difference between the percentages.

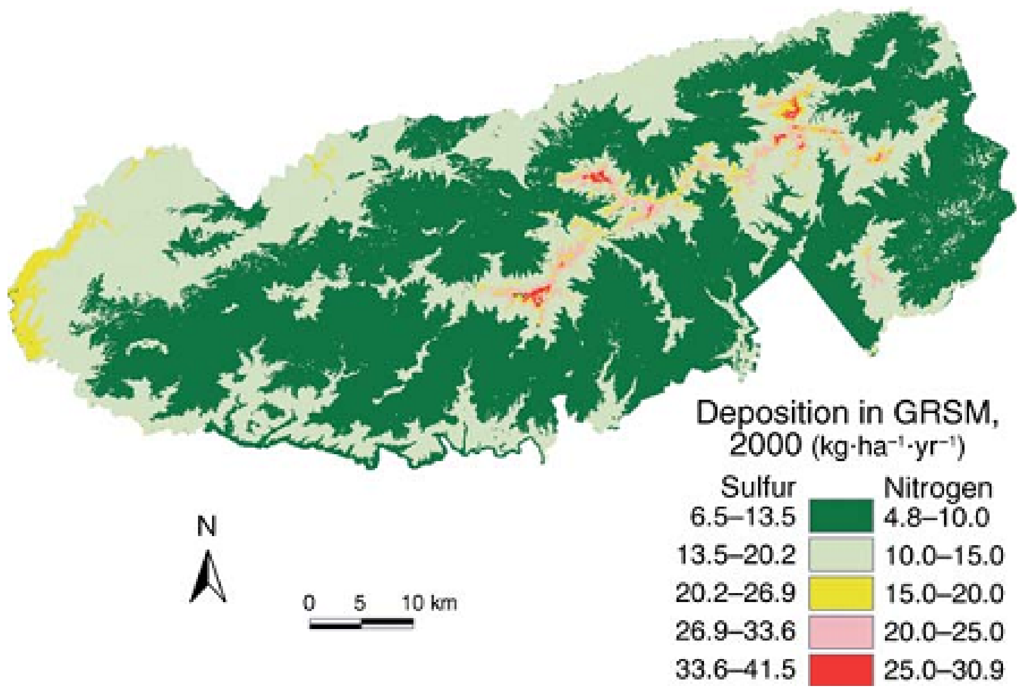

Figure 1.2: Modeled atmospheric deposition of N and S for the year 2000 and presented in Weathers et al. (2006).

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 try and strengthen the higher elevations. A cluster analysis was explored for the task but it was not successful, there was to much variation to cluster by elevation only. Therefore 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	114, 481, 482, 149, 66, 492, 137, 293, 270, 493, 485, 144, 224
4	914.4-1066.8 (3000-3500)	4	143, 142, 73, 71
5	1066.8-1371.6 (3500-4500)	4	74, 221, 251, 233
6	1371.6 < (4500 <)	2	253, 234

Table 1.3 contains all the sites of the 43 site survey that were not removed as influential, 36 sites are included in this table. 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 common way to asses 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. Recently, 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). And even 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. And 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 SO_4^{2-} 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

Water quality data is rarely perfectly formated 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 through out this paper: pH, ANC, NO_3^-, SO_4^{2-}. Each of these dependents are 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.

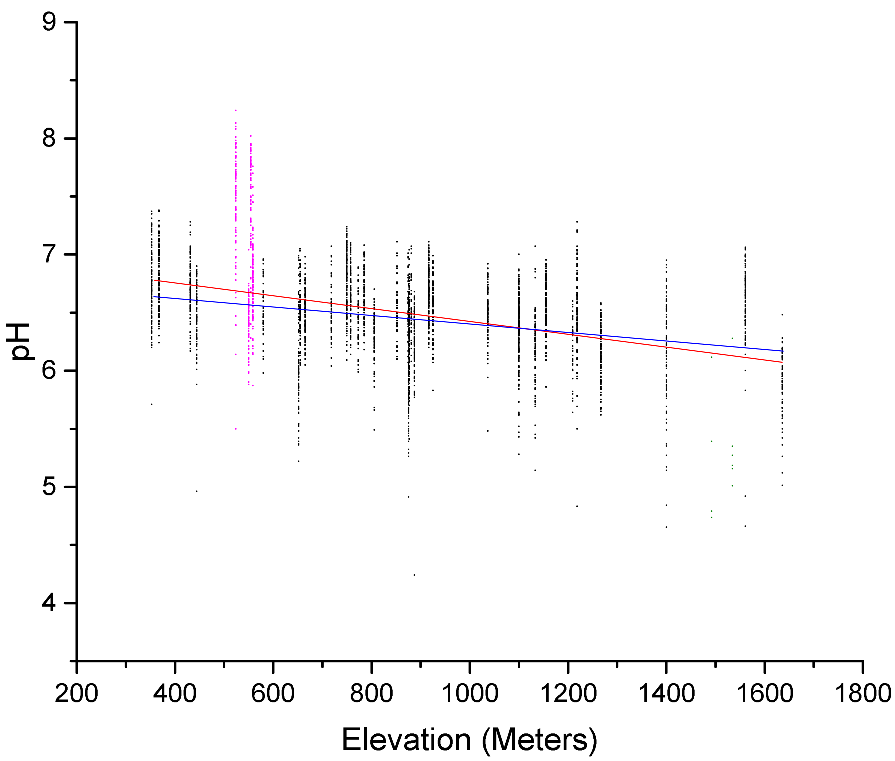

Figure 1.3: pH plotted vs. Elevation. With and without outliers.

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 contains 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 of the 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: Abrams creek watershed, sites that are affected by anakeesta geology, and stormflow (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 which are down hill of 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 very 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.

Stormflow is both influential and detrimental to GRSM water quality. Storms can bring high intensity rain fall, very quickly add pollutants from rain, storm runoff, and pollutants left in the soil.. Which in streams with already low ANC and pH can be very harmful to aquatic life. Along with measured ANC, measurements taken from stormflow can show uncharacteristically low pH values and high amounts of metals from leaching. In this way, stormflow 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 baseflow; 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 baselow/stormflow. If all stormflow observations are to be considered influential, the years 2011 and 2012 would need to be characterized. Quick analyses were run to see how influential stormflow was on the data as a whole, and it turned out that some were and many were not. Instead of throwing out all of the stormflow observations at once, single influential observations could be explained by stormflow and removed. They 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 assess whether conditions are improving or degrading, and to
- 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.
- Has 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, 4500¡)?
  - Time trends
  - Means Comparisons
- What is 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 following the two 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 dept. 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 (**?**). 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(**?**). The trend analysis of Robinson et al. (2008) used data from a 90 site survey while the trend analysis in **?** 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 common 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 before regression takes place. Much of the explained variation was handled in section 1.5 but some variation comes from single observations which are termed influential observations. Removal of excess variation is a normal process in step-wise 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 what made them influential. Modification or removal of an influential observation had to be justified, or it would remain an outlier. An example of modification of the data included a pH value that read 16.47 was changed to 6.47. Another example is that some conductivity values were obvious copies of the ANC value for the same observation. These conductivity values were removed. Some influential observations were not as obvious and 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 could be found, and attention would need be given to these also.

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 a F test statistic of .05 or greater 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 then the others were added. 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.

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 along side 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.

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

Table 2.1: Equations created through step-wise variable selection

Dependent (n)	Model	Adjusted r^2	Model p
pH (3116)	$.673 \times \log_2(\text{Sum Base Cations}) + (-.368 \times NO_3) + (.262 \times \text{Julian Day}) + (-.266 \times SO_4) + (-.050 \times \cos(\theta))$	0.630	<0.001
ANC (3116)	$(.415 \times \text{Sum Base Cations}) + (-.185 \times SO_4) + (.595 \times \text{Conductivity}) + (-.102 \times NO_3) + (.019 \times \text{Julian Date}) + (.005 \times Cl) + (.005 \times \sin(\theta))$	0.984	0.049
NO_3 (3116)	$(-.295 \times SO_4) + (-3.183 \times ANC) + (2.19 \times \text{Conductivity}) + (.923 \times \text{Sum Base Cations}) + (.120 \times \text{Julian Date}) + (.051 \times Cl) + (.047 \times \sin(\theta)) + (.031 \times \cos(\theta))$	0.498	0.017
SO_4 (3116)	$(-.166 \times NO_3) + (2.318 \times \text{Conductivity}) + (-3.229 \times ANC) + (1.033 \times \text{Sum Base Cations}) + (.042 \times \text{Julian Date})$	0.720	<0.001

trend as well. 144 different Julian date coefficients were calculated and are presented in two tables. Appendix D.1 records the Julian date coefficients calculated using the equations in Table 2.1 and appendix D.2 records the Julian date coefficients for equations containing only the three time variables. Each trend line is represented by its Julian date coefficient, the r^2 value for the trend line, and it's statistical significance.

Only 2 of the 72 trend lines in appendix D.1 are insignificant, while 50 of the 72 trend lines in appendix D.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 D.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 increasing 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 D.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 quite similar to those calculated in appendix D.1.

ANC

There are only two significant regression lines in for ANC in appendix D.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 D.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

The aim of Table 2.2 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.

Table 2.2: Dependents regressed against elevation (m) only.

set	Dependent	n	slope	r^2	per +1000m
1	pH	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	pH	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	pH	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

2.2.4 Results by Comparison

In comparing table 4 from Robinson et al. (2008) with appendix D.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 analysis 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. And 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 of 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 μeq 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 μeq L^{-1} per 1000-m elevation gain respectively. A comparison between these results and those reported in Table 2.2, In time set 3, both pH and ANC are significantly lower with trends of -.0286 pH units and -35.689 μeq L^{-1} per 1000-m gain 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 μeq L^{-1} between set 1 and set 2 in Table 2.2 and then by 6 μeq 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 μeq L^{-1} between set 1 and set 2 and then by almost 5 μeq L^{-1} between set 2 and set 3.

2.3 Discussion

It is interesting that the step-wise process did not choose elevation as an explanatory independent variable (X) for any of the dependents (Y), because many studies have declared elevation a significant explanation of variation and Figure 1.3 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 to small to show a significant elevation trend.

A time trend is also clearly evident with a simple plot of pH vs. time. But the mostly insignificant trends of appendix D.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), this study 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 Table B.1 are increasing through time along with pH. Which suggests desorption of SO_4^{2-} into the streams, thus raising the lower elevation SO_4^{2-} concentrations to meet the the higher concentrations of upper elevation sites that are more effected by acid deposition.

Chapter 3

Means Comparison

3.1 Methods

3.1.1 Introduction

- In the year 2008 scrubbers were installed into the Bullrun and kingston power plants
- These scrubbers significantly reduced the amount of SO_4 emitted by the smoke stacks of the power plants by **how much**
- A the same time an obvious decrease in measured SO_4 was discovered in the Stream Survey samples (UTK, 2012).
- The amount of SO_4 in the streams is thought to be (correlated with?) to the pH index of the streams when the SO_4 goes up the pH goes down.
- The hypothesis is that of the three sets of data containing water quality measurements from 1993 to 2012, if the data is broken at 2002 and 2008, that because of the obvious measured decrease in SO_4, there will be an obvious difference of means in the sets before and after 2008.
- This can be tested using an Analysis of Variance procedure.

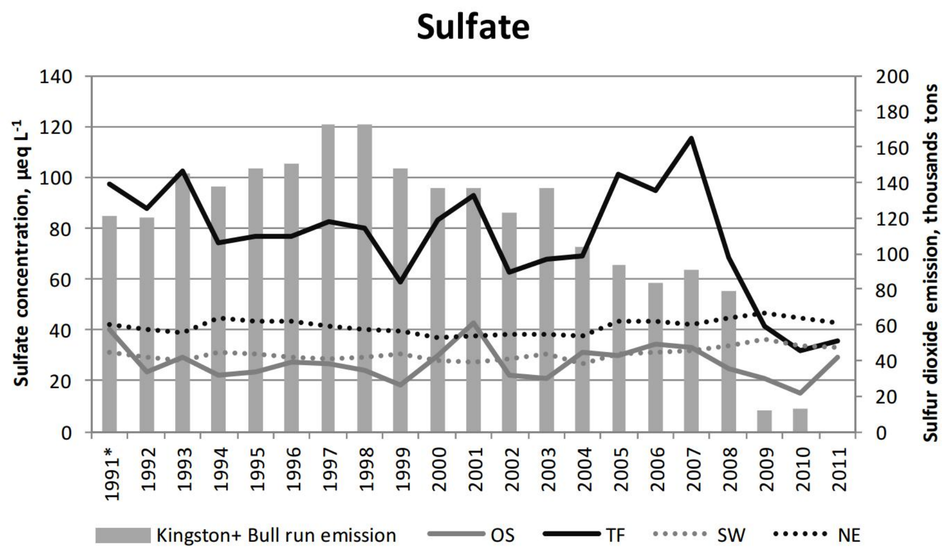

Figure 3.1: Sulfate emmisions of Kingstion and Bull run against those measured in Noland high elevation site.

- The data is only pH measurements for the three sets

  Instruments

  - The program used for this procedure was (probably SAS).
  - Heterscedasticity can be a problem a brown-forsythe test was employed to test for this.
  - If three groups are analyzed using ANOVA the only two outcomes may be "they are different" or "they are not different".
  - If they are not different then the analysis of the data is over.
  - If they are different then it would be nice to know which sets are different.

- This is accomplished with a Bonferoni analysis

3.1.2 Bonferoni Introduction

- Introduction from text book.

- rank-sum

  instruments

  - Bonferoni can output a graph presenting the means of each group in order to visually check for a difference in means. It will also output 95% confidence intervals between each pair of groups. This way definitive answers can be found for the question of "are they or are they not the same?"
  - Bonferoni assumptions
  - SAS

3.2 Results

- Background info?

- The output of the Bonferoni method includes 95% confidence intervals that represent definitive comparisons of the means of two groups of data. If the C.I. includes zero then the means are not statistically different.

- Table 3.1 reports the Bonferoni comparison means between the four water quality variables(pH, ANC, NO_3, SO_4) in one time set against the same water quality variable in another time set by elevation bands.

Table 3.1: Bonferoni comparisons between multiple groups

Elevation Classes	pH			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	$\neq$	$\neq$	$\neq$	$=$	$=$	$=$	$\neq$	$=$	$=$	$=$	$=$	$=$
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	$=$	$\neq$	$\neq$	$=$	$=$	$=$	$=$	$=$	$=$	$=$	$=$	$=$

- There are three groups compared in Table 3.1, they are the three time sets: 93-02, 03-08, 09-12. The table uses $=$ and $\neq$ to represent equality or inequality between the means of the groups compared.

- stuff from first draft

- the bonferoni analysis also outputs the results in figure form. These figures visually represent the group means and are presented in Figure **??** through Figure **??**.

- The negative trend of ANC is something to take note of.

3.3 Discussion

- Are these results a special case?

- Do these differences show up in other water quality analyses, not in the S.S.?

- What are the reasons that the means are higher or lower than expected?

- Differences between sets 2 and 3 were expected due to the scrubbers, did this occur?

- Why aren't the results as clear as the chart in the (**?**)?
  - probably math
- General hypothosis about what the results suggest
  - The results suggest that a larger difference is needed to see a sulfate difference between sets 2 and 3.

Chapter 4

Power Analysis

4.1 Methods

4.1.1 Introduction

- Statistics come with an inherent amount of error.
- The trend lines created in the trend analysis chapter have a defined error called type II error or β.
- β describes failure to reject a false null hypothesis or failure to detect a trend in the data when there really is one.
- β is usually described in terms of probability and it's opposite is called power(1-β)
- The power of a statistical test describes the probability that the test is true.
- The statistical test is the hypothesis test which tests if the coefficients of a regression line are zero. So whether or not a trend exists.
- The power of the trend lines will state the "truth" of the slope of the trend. A trend lilne with a power of 1.00 means that there is a 100% chance that the calculated slope is not zero.

- Using the earlier calculated trend lives as input, the power of each regression line was calculated with the help of G*power. An a priori analysis was calculated to help determine the number of samples needed for desired levels of power.

4.1.2 Body

- The objectives of the power analysis are to determine the power of the trend lines calculated from past observations and to determine an adaquate number of samples needed for different levels of power for the future.

- The inputs needed in the G*power program for a post hoc analysis are: number of observations (N), adjusted r^2, number of predictors, and Effect size. N and adj.r^2 are outputs from the trend analysis and effect size is calculated using G*power. These values are reported in Table F.1 and Table F.2.

- A post hoc analysis of the trend line data from Table F.2 is not useful. This is because most of the lines have terribly low r^2 values and are insignificant trend lines. The power of an insignificant trend line is also insignificant.

- Post hoc analysis and a priori were run on both methods for trend lines

- G*power is a free power analysis program written by four germen psychology professors.

- It runs the gamut in power analysis options and uses methods stated in (Cohen, 1992).

- G*power was used to calculate powers in the post hoc analysis and sample sizes for the a priori analysis.

- Excel was used along with results provided by G*power to create scenarios to finish up the a priori analysis.

4.1.3 Procedures

Post hoc

- Data compiled in Table F.1 and Table F.2 give the inputs required for a post hoc power analysis on th previously created trend lines.
- required inputs for G*power include, ES(Effect Size), α(alpha), number of observations, and number of predictors.
  - ES is calculated in G*power by the Cohen method stated in (Cohen, 1992) "A Power Primer".
  - Alpha refers to the α of the trend lines (.05).
  - Number of observations is given in trend line output from SPSS.
  - Number of predictors is also stated in trend line output.
- The calculate button will calculate the power
  - This is all that is needed for a post hoc analysis. It answers the question "What was the power of the survey ?" or "How strong are the trend lines that were computed?"
- The calculated powers are reported along side their trend line inputs in Table F.1 and Table F.2.

A priori

- The a priori analysis can help survey planners to create a sampling survey that will produce trend lines with certain ES values and powers.
- There are two objectives to this analysis which are to create "power graphs", which are plots of power vs. sample size. The other is to plan out an actual scenario for which samples can be added or subtracted to elevation bands for a desired power of .80 and an ES of .15.

- The power graphs are created in G*power using the "x-y plot for a range of values" button next to the "calculate" button.

- They-axis has the power values while the x-axis contains the number of observations or samples. The power will increase with number of samples until it reaches 100.

- Four power graphs were created, one for each water quality variable. If ES and power are set to .15 and .80 respectively for every presumed trend line then the only variable is number of predictors. The number of predictors is set for each water quality variable (pH, ANC, NO_3,SO_4). Taken from the earlier step-wise selection method (link to step-wise table). Therefore only one "power graph" is needed for every trend line in each variable.

- ES and power can be chosen or kept constant based on reports by Cohen.

- Cohen's standardizations

- While the "power graphs" are useful in planning for the future of the stream survey, it can be shown that if ES and power are chosen, exact numbers of samples and sites can be added and subtracted from elevation bands.

Table 4.1: A priori calculation in G*power when alpha, ES, and power are set to .05, .15, and .80 respectively.

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

- The rest was done in excel

- This calculated number of observations can be divided by the number of samples collected in one year to get the number of years required to reach a power of .80.

- The analysis can be further conducted by calculating the number of samples per year to achieve a power of .80. For this calculation all water quality variables were given the highest number of samples of 110 and 77 was used for the trends using only time variables.

Table 4.2: 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

- **??** is needed to calculate number of samples needed per elevation band to achieve a power of .80. This number of samples can then be further divided to get a number of sites needed to achieve a power of .80. If a trend line with a power of .80 is desired after one year ,for all water quality variables to be satisfied, 110 samples need to be collected. If four years are waited then only 28 samples need to be collected per year.

- To create this final table the number of samples per elevation band was subtracted from the number of samples to achieve a power of .80 which gives us the number of samples needed in addition to what is currently collected to receive a power of .80. These results are organized into samples needed per elevation band to achieve a power of .80 and seperated by years depending of how many years of data go into the trend lines.

4.2 Results

4.2.1 Post hoc

- A post hoc power analysis was conducted for each of the two methods of trend analysis.

- Table F.1 and Table F.2 record the results of the post hoc analysis on the trend lines with variables created through the step-wise method and the trend lines created using only time variables respectively. Included in these tables are the number of samples and r^2 variables from the trend analysis and effect size and power from the post hoc analysis.

- Table F.1 and Table F.2 are broken into the four analyzed water quality variables (pH, ANC, NO_3,SO_4) and divided into the tree time sets (93-02, 03-08, 09-12), and then further divided into the six elevation classes.

- use results from previous draft

- any similar power analysis?

4.2.2 A priori

Power graphs

- The results of the a priori power analysis will be the most important for planning.

- The usual output is the "power graph" which plots power on the y-axis and total sample size on the x-axis.

- G*power outputs some very nice power graphs. The power graphs created from the a priori power analysis are presented in Figure G.1, Figure G.2, Figure G.3, and Figure G.4.

- There were four power graphs created, three for the water quality variables and one for the time variables. ANC and Nitrate both have the same number of predictors from the step-wise variable selection method and therefore create the same power graph.

- each graph contains 3 lines representing 3 different ES choices: .15, .25, and .35. These were chosen to mimic the choices of small, medium, and large effects standardized by Cohen in (Cohen, 1992). Limitations of the G*power program left the best choices to be .15, .25, and .35. A small effect of .02 was ignored because preliminary graph results showed it to be not useful.

Planning with power analysis

- Using the ability of the a priori power analysis to compute a number of samples needed for a certain power, a scenario was played out to see how many sites needed to be added or could be removed from an elevation band in the stream survey.

Table 4.3: Years to acheive a power of .80

Elevation Bands	Site #	Current n/yr	pH	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, 483, 147, 148, 484	34	2.88	3.21	3.03	2.26
3	114, 481, 482, 149, 66, 492, 137, 293, 270, 493, 485, 144, 224	62	1.58	1.76	1.66	1.24
4	143, 142, 73, 71	24	4.08	4.54	4.29	3.21
5	74, 221, 251, 233	22	4.45	4.95	4.68	3.50
6	253, 234	12	8.17	9.08	8.58	6.42

- This scenario was followed through with both methods of trend lines.

- **??** 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 was tabulated. The values in the remaining columns were calculated by dividing the number of samples given in **??** by the current samples per year column in **??**.

- Looking at the table there are 26 samples collected in elevation band one in one year. In order to compute a trend line that receives a power of .80 with pH as the dependent samples would need to be collected for 3.77 years before the trend line is computed. The larges is elevation class for a trend line in ANC or NO_3 which requires 9.08 years.

Table 4.4: Necesary 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 4.5: Necesary 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

- The left side of both **??** and **??** show how many more samples are required to get a trend line with a power of .80.

- In ?? for elevation class 3, 48 more samples need to be collected if a trend line 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.
- ?? works the same way as ?? but of course it uses different variables for the trend lines.
- results from previous draft
- any other papers like this?

4.3 Discussion

4.3.1 Post hoc

- The results presented in Table F.1 and Table F.2 show how the calculated power is highly affected by number of observations more than anything else.
- In Table F.1, even when the r^2 and ES values are relatively low if the N is greater than 100 then the power is excellent.
- Table F.2 show the effect of the ES on power. Other than these lines being insignificant, many of the ES values are small according to Cohen and when compared to Table F.1. Low ES values and low observations create low powers. Low ES values com from low r^2 values. The low r^2 values can be blamed for the insignificance of the lines and the poor powers.
- Some lines are just not well described by Julian Date,$\sin(\theta)$, and $\cos(\theta)$ only.

4.3.2 A priori

- How can these results be used?

- How can these results be manipulated?
- The results in Table 4.4 and Table 4.5 can help with both of the problems of The park wanting a cheaper survey and researchers wanting more high elevation sites.
- The table can be used to re-organize sites across bands.
  - In the current SS scheme there is a surplus of sites in lower elevation bands and a deficit for sites in higher elevations.
  - Looking at the right side of Table 4.4, if trends are desired after four years of data with a power of .80 and an ES of .15, seven sites may be taken from elevation bands 2 and 3 and 5 would need to be added to elevation bands 4,5, and 6.
  - After this re-arrangement two sites may be completely discontinued.
  - This saves time, effort, and money, but it is a very specific scenario.
- The downside of an a priori power analysis is that once you pick all the variables that go into it, you can' t change them in the future
  - Variables that can change include how you divide the sites into elevation bands
  - Trend line creation (alpha, variable selection)
  - Power analysis (power, and ES)
- If during the hypothetical situation in which four years are waited to do another trend analysis, a better model is found, then the survey would need to be re-evaluated to reflect the new model.
  - the model could require a different number of sites
- Choices for power and ES could change

- planning with the a priori power analysis requires guessing the trends for the future.
- This guess will probably be based on the past , such as this one.
- This guess assumes that trends of the past will continue into the future
- The ANOVA/Bonferoni and the comparison between (Robinson et al., 2008) and the current trends shows that this is difficult.
- better understanding is needed
- At the end of the day the trends are positive!

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Appendix

Appendix A

A.1 Site Data

A.2 Site data

	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.1: GRSM Stream Survey site descriptions

	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

Table A.2: Site Data

Appendix B

Descriptive Statistics

Table B.1: Descriptive statistics of Water Quality in the GRSM

Set	Class	pH				ANC meql				Nitrate meql				Sulfate meql			
		N	Minimum	Maximum	Mean	N	Minimum	Maximum	Mean	N	Minimum	Maximum	Mean	N	Minimum	Maximum	Mean
1993-2002																	
	1	327	4.96	7.90	6.57	327	-20.74	1534.47	149.76	275	0.00	49.94	12.04	325	12.32	85.01	36.09
	2	393	5.32	7.00	6.25	392	-7.43	182.95	40.75	377	1.37	73.76	26.62	390	0.00	159.51	51.68
	3	400	4.65	8.24	6.44	398	-19.97	1624.49	158.44	365	0.00	96.13	26.14	391	0.00	262.37	54.00
	4	121	6.18	7.11	6.50	120	24.45	178.00	75.84	105	2.16	28.29	11.90	119	12.34	77.74	25.16
	5	116	6.07	7.05	6.50	116	41.34	162.76	77.06	66	1.23	10.55	4.35	116	7.51	79.98	26.14
	6	110	5.77	7.06	6.41	110	15.64	165.02	68.01	81	1.56	60.46	21.13	110	14.71	61.16	28.35
2003-2008																	
	1	255	5.22	7.95	6.65	255	-37.09	1314.56	173.48	252	0.50	62.75	16.56	261	10.00	93.23	38.85
	2	289	4.83	7.07	6.32	289	-1.88	145.95	42.20	296	0.62	67.12	29.20	298	11.64	152.55	48.19
	3	299	4.65	8.10	6.55	299	-26.45	1591.06	172.82	297	0.13	95.72	27.69	308	10.44	490.01	54.25
	4	119	5.95	7.06	6.58	119	23.36	128.28	69.90	121	1.87	55.67	17.51	123	13.88	61.31	29.04
	5	35	5.98	7.03	6.50	35	36.37	115.80	77.84	30	1.45	26.48	7.59	37	12.18	117.46	30.54
	6	97	5.79	7.05	6.44	97	6.73	130.63	55.68	98	1.09	72.79	24.88	101	10.02	65.53	34.31
209-2012																	
	1	191	5.42	8.02	6.77	191	-0.02	1377.93	164.72	191	0.22	62.14	16.31	190	14.61	113.83	39.63
	2	212	4.91	7.28	6.47	212	-11.74	174.52	44.45	212	4.43	72.17	30.08	212	13.45	125.36	47.41
	3	228	4.73	7.96	6.68	228	-18.28	1535.69	160.14	228	1.04	72.16	26.23	228	13.59	317.63	58.15
	4	97	6.20	7.08	6.68	97	25.70	107.58	64.13	97	0.54	34.67	18.72	97	19.89	46.66	29.33
	5	29	6.30	7.11	6.77	29	40.10	115.94	73.55	29	0.21	83.68	6.44	29	16.78	109.18	36.16
	6	76	4.24	7.09	6.52	76	-3.92	114.28	46.15	76	0.16	79.04	32.17	76	15.72	63.32	37.05

Appendix C

Variable selection

Table C.1: 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	pH	ANC	NO_3	SO_4
pH	Dependent				
ANC	Dependent			X	X
NO_3	Dependent	X	X		X
SO_4	Dependent	X	X	X	
Julian Date			X	X	X
Month					
Year					
Julian Date Days	Seasonality	X			
$\sin(\theta)$	Seasonality	O	X	X	O
$\cos(\theta)$	Seasonality	X	O	X	O
Sum Base Cations			X	X	X
Conductivity			X	X	X
Chloride			X	X	
Elevation (m)					
Slope					
$\log_2$ (ANC)					
$\log_2$ (Base Cations)		X			
Number of predictors		6	8	8	7

Appendix D

Julian Date Coefficients

D.1 Step-wise Method

D.2 Temporal Variables

Table D.1: Time trend results for specific elevation classes using variables from step-wise regression. **Bold** results are insignificant.

Time set	Elevation class	Elevation range m (ft)	Number of sites	Julian date coefficient, eq/L or pH units (model adjusted r^2) (p-value)			
				pH	ANC	Nitrate	Sulfate
1993-2002	1	304.8-609.6	5	0.069	0.007	0.034	-0.096
		(1000-2000)		0.712	0.985	0.503	0.569
				0.000	0.000	0.000	0.000
	2	609.6-762	9	-0.091	-0.036	-0.037	0.019
		(2000-2500)		0.388	0.603	0.699	0.766
				0.000	0.000	0.000	0.000
	3	762-914.4	13	-0.010	0.008	-0.013	0.024
		(2500-3000)		0.693	0.971	0.359	0.590
				0.000	0.000	0.000	0.000
	4	914.4-1066.8	4	0.019	0.015	0.058	0.061
		(3500-3500)		0.205	0.709	0.410	0.402
				0.000	0.000	0.000	0.000
	5	1066.8-1371.6	4	-0.157	-0.082	0.288	-0.133
		(3500-4500)		0.165	0.760	0.328	0.566
				0.010	0.000	0.000	0.000
	6	1371.6<	2	0.218	0.067	-0.011	0.092
		(4500<)		0.505	0.802	0.871	0.716
				0.000	0.000	0.000	0.000
2003-2008	1	304.8-609.6	5	0.150	-0.004	0.038	0.039
		(1000-2000)		0.781	0.996	0.551	0.673
				0.000	0.000	0.000	0.000
	2	609.6-762	9	0.275	0.033	0.044	0.044
		(2000-2500)		0.348	0.779	0.816	0.893
				0.000	0.000	0.000	0.000
	3	762-914.4	13	0.156	0.005	0.072	0.034
		(2500-3000)		0.663	0.996	0.637	0.923
				0.000	0.000	0.000	0.000
	4	914.4-1066.8	4	0.249	-0.028	0.092	0.110
		(3500-3500)		0.400	0.779	0.405	0.343
				0.000	0.000	0.000	0.000
	5	1066.8-1371.6	4	0.137	-0.020	0.204	0.135
		(3500-4500)		0.300	0.739	0.562	0.884
				0.027	0.000	0.001	0.000
	6	1371.6<	2	0.359	0.127	0.074	0.161
		(4500<)		0.317	0.812	0.832	0.844
				0.000	0.000	0.000	0.000
2009-2012	1	304.8-609.6	5	0.106	-0.002	0.026	-0.052
		(1000-2000)		0.894	0.989	0.376	0.536
				0.000	0.000	0.000	0.000
	2	609.6-762	9	0.218	0.069	0.121	0.039
		(2000-2500)		0.606	0.862	0.735	0.887
				0.000	0.000	0.000	0.000
	3	762-914.4	13	0.056	0.007	0.019	0.050
		(2500-3000)		0.766	0.997	0.598	0.915
				0.000	0.000	0.000	0.000
	4	914.4-1066.8	4	0.413	-0.006	-0.013	-0.068
		(3500-3500)		0.593	0.772	0.635	0.529
				0.000	0.000	0.000	0.000
	5	1066.8-1371.6	4	**-0.115**	0.901	**0.098**	0.015
		(3500-4500)		**0.158**	0.540	**-0.272**	0.658
				0.130	0.001	**0.975**	0.000
	6	1371.6<	2	0.289	0.059	0.097	-0.059
		(4500<)		0.286	0.809	0.881	0.861
				0.000	0.000	0.000	0.000

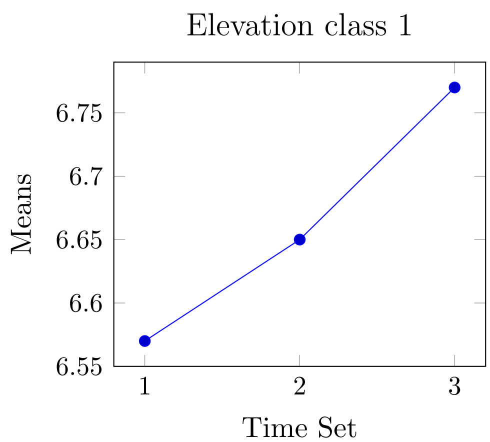
Table D.2: Time trend results for specific elevation classes using julian date, cosine(θ), and sine(θ) only. **Bold** results are insignificant.

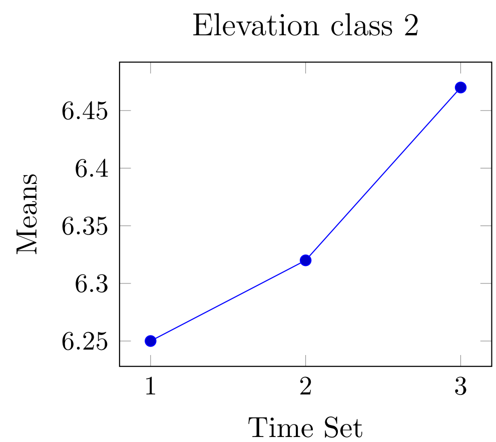
Time set	Elevation class	Elevation range m (ft)	Number of sites	Julian date coefficient, eq/L or pH units (model adjusted r^2) (p-value)			
				pH	ANC	Nitrate	Sulfate
1993-2002	1	304.8-609.6 (1000-2000)	5	**0.054** **0.047** **0.321**	**0.089** **0.024** **0.106**	-0.138 0.016 0.022	-0.190 0.045 0.001
	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** **.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** **.100**	-0.148 0.381 0.047	0.330 0.120 0.006	**0.092** **-0.010** **0.331**
	6	1371.6< (4500<)	2	**.156** **.096** **.092**	**-0.016** **0.075** **0.863**	**-0.208** **0.092** **0.058**	**-0.036** **-0.009** **0.707**
2003-2008	1	304.8-609.6) (1000-2000	5	.139 0.040 0.025	**0.009** **0.001** **0.888**	0.155 0.061 0.012	0.192 0.043 0.002
	2	609.6-762 (2000-2500)	9	0.145 0.061 0.012	**-0.090** **0.081** **0.114**	0.178 0.043 0.002	0.138 0.014 0.017
	3	762-914.4 (2500-3000)	13	**0.103** **0.020** **0.075**	**-0.006** **-0.003** **0.925**	**0.047** **-0.003** **0.418**	**0.099** **0.006** **0.085**
	4	914.4-1066.8 (3500-3500)	4	0.235 0.148 0.007	**-0.029** **0.180** **0.728**	0.193 0.086 0.030	0.192 0.023 0.035
	5	1066.8-1371.6 (3500-4500)	4	**0.135** **-0.069** **0.466**	**-0.112** **0.337** **0.443**	**-0.176** **-0.082** **0.401**	**0.067** **-0.024** **0.701**
	6	1371.6< (4500<)	2	0.204 0.081 0.041	**-0.108** **0.094** **0.274**	0.236 0.046 0.020	0.307 0.074 0.002
2009-2012	1	304.8-609.6 (1000-2000)	5	**0.111** **0.028** **0.122**	**0.026** **0.000** **0.718**	**-0.036** **0.018** **0.619**	**-0.092** **0.005** **0.207**
	2	609.6-762 (2000-2500)	9	0.141 0.052 0.037	**0.017** **0.056** **0.800**	**0.020** **0.011** **0.767**	**-0.062** **-0.010** **0.376**
	3	762-914.4 (2500-3000)	13	**-0.034** **-0.009** **0.611**	**-0.027** **-0.002** **0.684**	**-0.036** **-0.004** **0.592**	**0.078** **-0.007** **0.246**
	4	914.4-1066.8 (3500-3500)	4	0.405 0.200 0.000	**0.032** **0.161** **0.733**	**-0.067** **-0.016** **0.518**	**-0.129** **-0.011** **0.215**
	5	1066.8-1371.6 (3500-4500)	4	**-0.031** **0.218** **0.934**	0.891 0.466 0.007	**0.052** **-0.039** **0.904**	**-0.414** **-0.076** **0.347**
	6	1371.6< (4500<)	2	0.264 0.039 0.023	**0.083** **0.058** **0.462**	**-0.021** **-0.016** **0.859**	**-0.214** **0.007** **0.068**

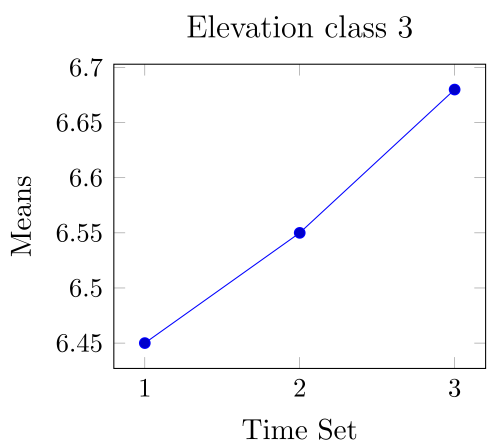
Appendix E

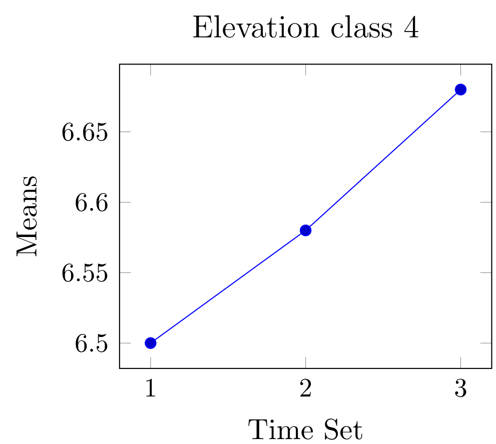
ANOVA/Bonferoni

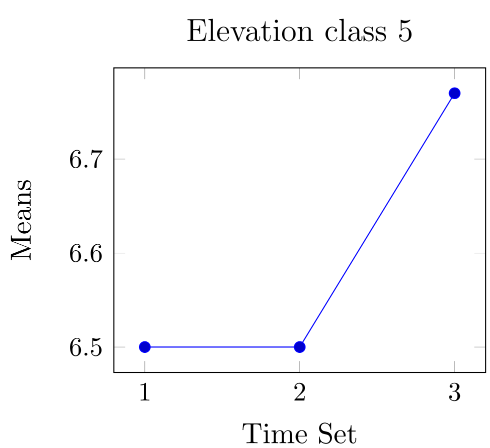
E.1 pH

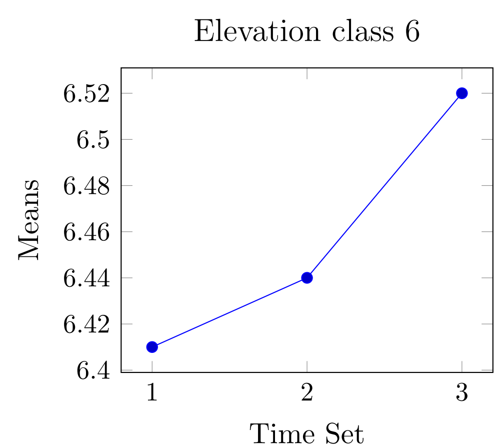

Elevation class 1
Means
6.55
6.6
6.65
6.7
6.75
1
2
3
Time Set


Elevation class 2
Means
6.25
6.3
6.35
6.4
6.45
1
2
3
Time Set

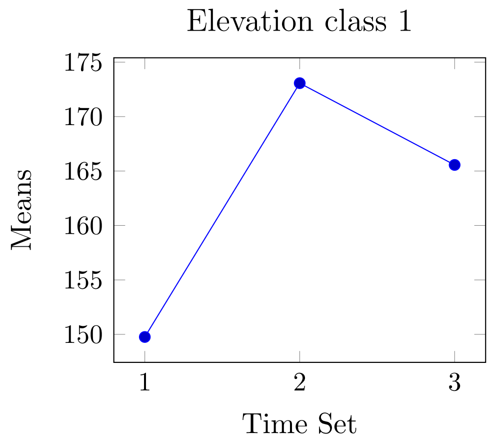

Elevation class 3
Means
6.45
6.5
6.55
6.6
6.65
6.7
1
2
3
Time Set

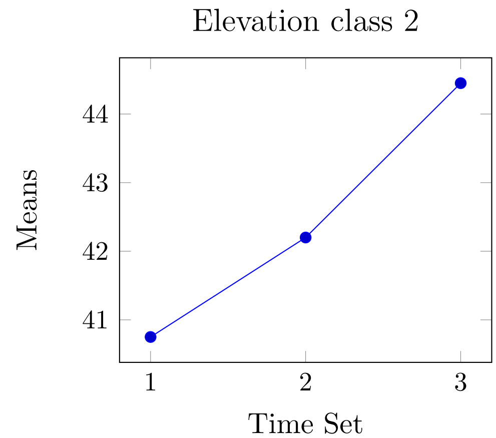

Elevation class 4
Means
6.5
6.55
6.6
6.65
1
2
3
Time Set

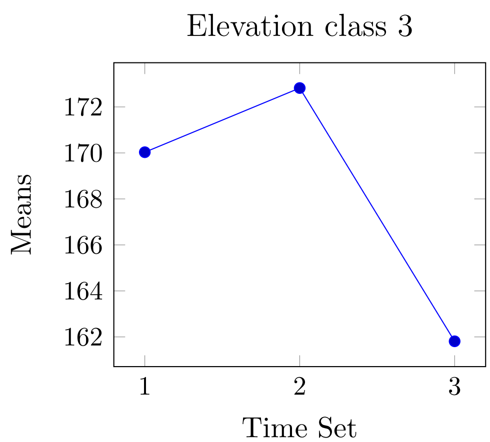

Elevation class 5
Means
6.5
6.6
6.7
1
2
3
Time Set

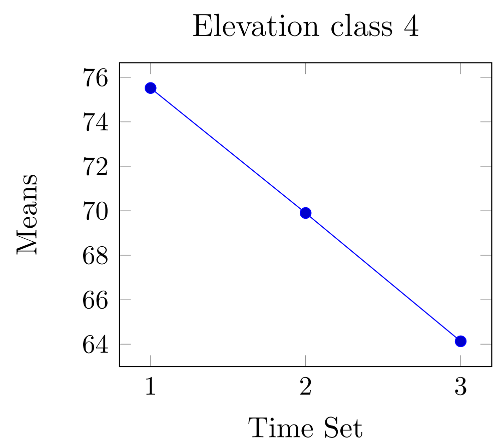

Elevation class 6
Means
6.4
6.42
6.44
6.46
6.48
6.5
6.52
1
2
3
Time Set

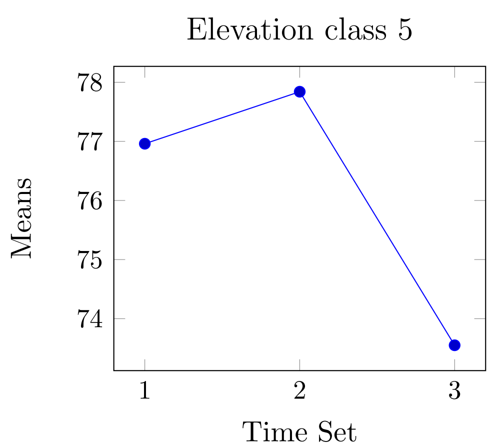
E.2 ANC

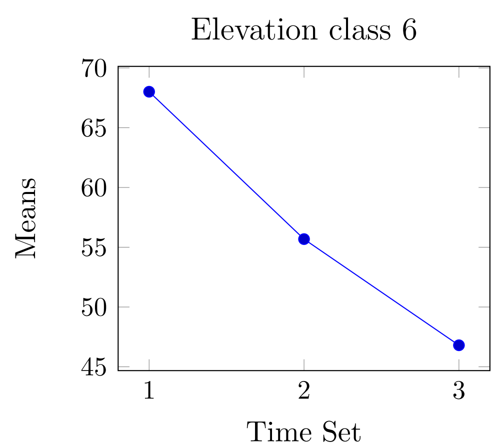

Elevation class 1
175
170
165
160
155
150
Means
1
2
3
Time Set


Elevation class 2
44
43
42
41
Means
1
2
3
Time Set

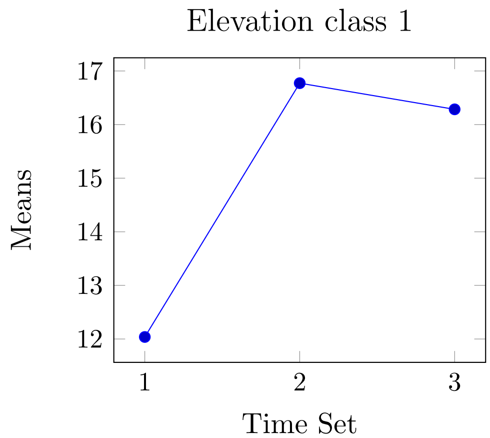

Elevation class 3
172
170
168
166
164
162
Means
1
2
3
Time Set

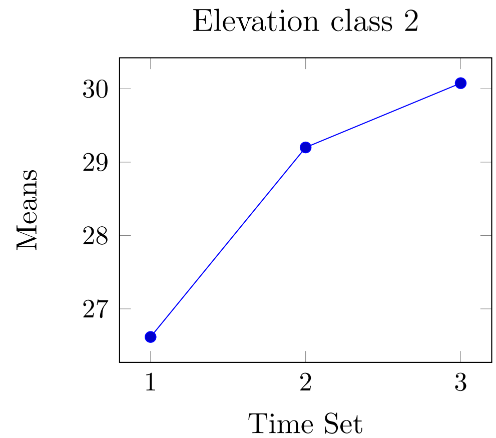

Elevation class 4
76
74
72
70
68
66
64
Means
1
2
3
Time Set

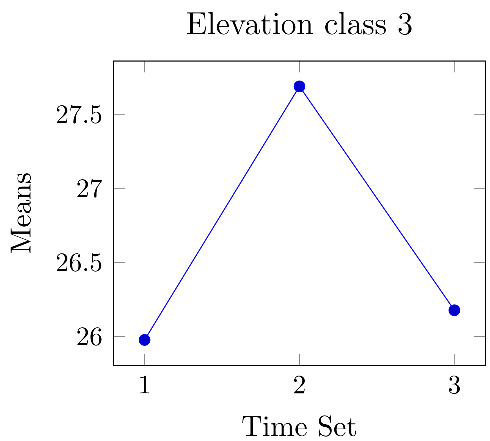

Elevation class 5
78
77
76
75
74
Means
1
2
3
Time Set

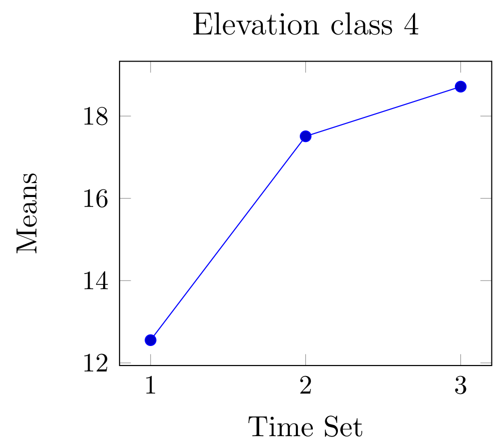

Elevation class 6
70
65
60
55
50
45
Means
1
2
3
Time Set

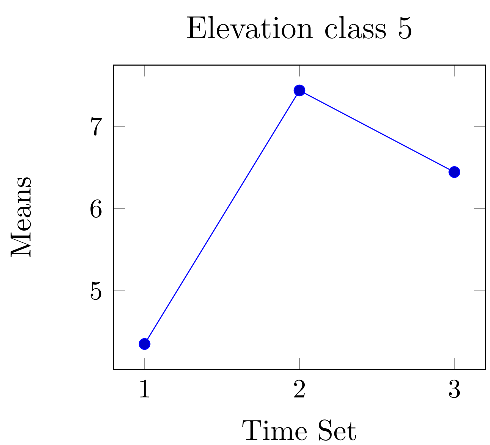
E.3 Nitrate

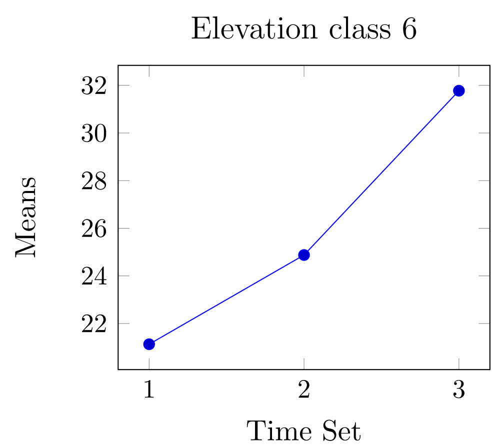

Elevation class 1
Means
17
16
15
14
13
12
1
2
3
Time Set


Elevation class 2
Means
30
29
28
27
1
2
3
Time Set

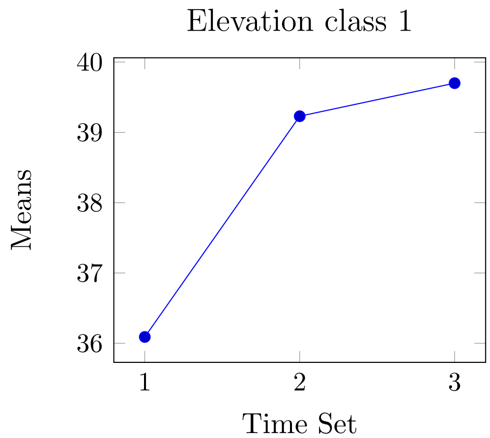

Elevation class 3
Means
27.5
27
26.5
26
1
2
3
Time Set

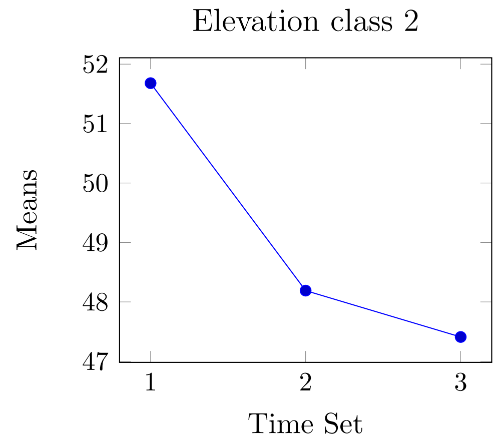

Elevation class 4
Means
18
16
14
12
1
2
3
Time Set

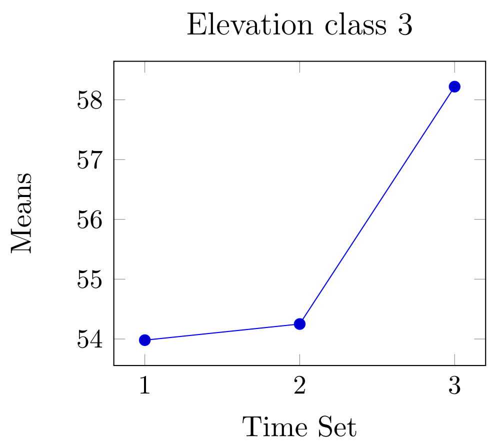

Elevation class 5
Means
7
6
5
1
2
3
Time Set

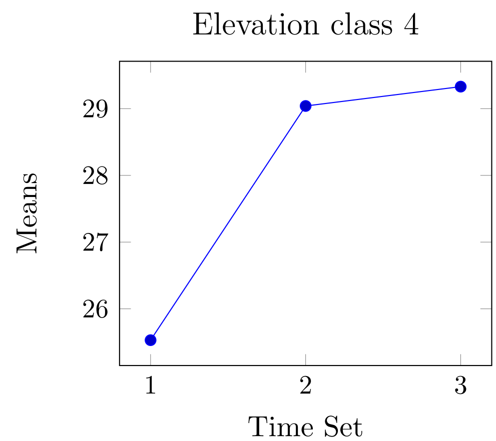

Elevation class 6
Means
32
30
28
26
24
22
1
2
3
Time Set

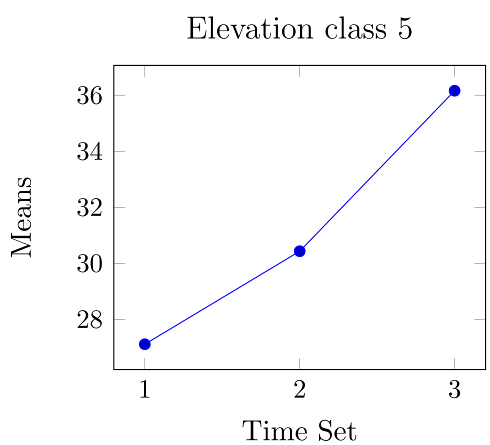
E.4 Sulfate

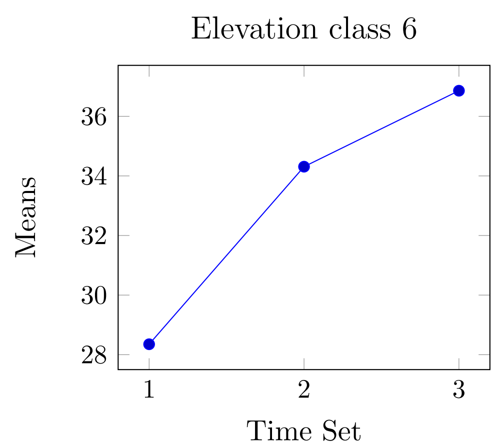

Elevation class 1
Means
36
37
38
39
40
1
2
3
Time Set


Elevation class 2
Means
47
48
49
50
51
52
1
2
3
Time Set


Elevation class 3
Means
54
55
56
57
58
1
2
3
Time Set


Elevation class 4
Means
26
27
28
29
1
2
3
Time Set


Elevation class 5
Means
28
30
32
34
36
1
2
3
Time Set


Elevation class 6
Means
28
30
32
34
36
1
2
3
Time Set

Appendix F

Post Hoc Power Analsysis

F.1 Step-Wise Variables

F.2 Temperol variables

Table F.1: Post hoc power analysis using G*power and a calculated ES, alpha is .05. **Bold** results are insignificant.

		pH				ANCmeqL				NitratemeqL				SulfatemeqL			
Set	Class	N	Adjusted r^2	Effect Size	Actual Power	N	Adjusted r^2	Effect Size	Actual Power	N	Adjusted r^2	Effect Size	Actual Power	N	Adjusted r^2	Effect Size	Actual Power
1993-2002																	
	1	327	0.712	2.47	1.00	327	0.985	65.67	1.00	275	0.503	1.01	1.00	325	0.569	1.32	1.00
	2	393	0.388	0.63	1.00	392	0.603	1.52	1.00	377	0.699	2.32	1.00	390	0.766	3.27	1.00
	3	400	0.693	2.26	1.00	398	0.971	33.48	1.00	365	0.359	0.56	1.00	391	0.590	1.44	1.00
	4	121	0.205	0.26	0.99	120	0.709	2.44	1.00	105	0.410	0.69	1.00	119	0.402	0.67	1.00
	5	116	0.165	0.20	0.96	116	0.760	3.17	1.00	66	0.328	0.49	0.98	116	0.566	1.30	1.00
	6	110	0.505	1.02	1.00	110	0.802	4.05	1.00	81	0.871	6.75	1.00	110	0.716	2.52	1.00
2003-2008																	
	1	255	0.781	3.57	1.00	255	0.996	249.00	1.00	252	0.551	1.23	1.00	261	0.673	2.06	1.00
	2	289	0.348	0.53	1.00	289	0.779	3.52	1.00	296	0.816	4.43	1.00	298	0.893	8.35	1.00
	3	299	0.663	1.97	1.00	299	0.996	249.00	1.00	297	0.637	1.75	1.00	308	0.923	11.99	1.00
	4	119	0.400	0.67	1.00	119	0.779	3.52	1.00	121	0.405	0.68	1.00	123	0.343	0.52	1.00
	5	35	0.300	0.43	0.74	35	0.739	2.83	1.00	30	0.562	1.28	0.98	37	0.884	7.62	1.00
	6	97	0.317	0.46	1.00	97	0.812	4.32	1.00	98	0.832	4.95	1.00	101	0.844	5.41	1.00
2009-2012																	
	1	191	0.894	8.43	1.00	191	0.989	89.91	1.00	191	0.376	0.60	1.00	190	0.536	1.16	1.00
	2	212	0.606	1.54	1.00	212	0.862	6.25	1.00	212	0.735	2.77	1.00	212	0.887	7.85	1.00
	3	228	0.766	3.27	1.00	228	0.997	332.33	1.00	228	0.598	1.49	1.00	228	0.915	10.76	1.00
	4	97	0.593	1.46	1.00	97	0.772	3.39	1.00	97	0.635	1.74	1.00	97	0.529	1.12	1.00
	5	29	**0.158**	0.19	0.28	29	0.540	1.17	0.96	29	**-0.272**	NA	NA	29	0.658	1.92	1.00
	6	76	0.286	0.40	0.99	76	0.809	4.24	1.00	76	0.881	7.40	1.00	76	0.861	6.19	1.00

Table F.2: Post hoc power analysis using G*power a calculated ES, an alpha of .05 with the variables: sine(θ), cosine(θ), and julian date only. **Bold** results are insignificant.

		pH				ANCmeqL				NitratemeqL				SulfatemeqL			
Set	Class	N	Adjusted r^2	Effect Size	Actual Power	N	Adjusted r^2	Effect Size	Actual Power	N	Adjusted r^2	Effect Size	Actual Power	N	Adjusted r^2	Effect Size	Actual Power
1993-2002																	
	1	327	**0.047**	0.049	0.93	327	**0.024**	0.02	0.65	275	0.016	0.02	0.39	325	0.045	0.05	0.92
	2	393	**0.128**	0.15	1.00	392	**0.189**	0.23	1.00	377	**0.017**	0.02	0.55	390	**0.009**	0.01	0.32
	3	400	**0.013**	0.01	0.46	398	**0.000**	0.00	0.06	365	**-0.004**	NA	NA	391	**-0.004**	NA	NA
	4	121	**0.059**	0.06	0.61	120	**0.294**	0.42	1.00	105	**-0.027**	NA	NA	119	**-0.016**	NA	NA
	5	116	**0.051**	0.05	0.52	116	0.381	0.62	1.00	66	0.120	0.14	0.68	116	**-0.010**	NA	NA
	6	110	**0.096**	0.11	0.81	110	**0.075**	0.08	0.69	81	**0.092**	0.10	0.64	110	**-0.009**	NA	NA
2003-2008																	
	1	255	0.040	0.04	0.78	255	**0.001**	0.00	0.07	252	0.061	0.06	0.94	261	0.043	0.04	0.82
	2	289	0.061	0.06	0.96	289	**0.081**	0.09	0.99	296	0.043	0.04	0.87	298	0.014	0.01	0.37
	3	299	**0.020**	0.02	0.52	299	**-0.003**	NA	NA	297	**-0.003**	NA	NA	308	**0.006**	0.01	0.18
	4	119	0.148	0.17	0.97	119	**0.180**	0.22	0.99	121	0.086	0.09	0.80	123	0.023	0.02	0.26
	5	35	**-0.069**	NA	NA	35	**0.337**	0.51	0.93	30	**-0.082**	NA	NA	37	**-0.024**	NA	NA
	6	97	0.081	0.09	0.67	97	**0.094**	0.10	0.74	98	0.046	0.05	0.40	101	0.074	0.08	0.64
2009-2012																	
	1	191	**0.028**	0.03	0.47	191	**0.000**	0.00	0.05	191	**0.018**	0.02	0.31	190	**0.005**	0.01	0.11
	2	212	0.052	0.05	0.82	212	**0.056**	0.06	0.85	212	**0.011**	0.01	0.22	212	**-0.010**	NA	NA
	3	228	**-0.009**	NA	NA	228	**-0.002**	NA	NA	228	**-0.004**	NA	NA	228	**-0.007**	NA	NA
	4	97	0.200	0.25	0.99	97	**0.161**	0.19	0.96	97	**-0.016**	NA	NA	97	**-0.011**	NA	NA
	5	29	**0.218**	0.28	0.58	29	0.466	0.87	0.98	29	**-0.039**	NA	NA	29	**-0.076**	NA	NA
	6	76	0.039	0.04	0.27	76	**0.058**	0.06	0.39	76	**-0.016**	NA	NA	76	**0.007**	0.01	0.08

Appendix G

A priori analysis

G.1 Power graphs

G.1.1 pH

G.1.2 ANC and Nitrate

G.1.3 Sulfate

G.1.4 Time Variables

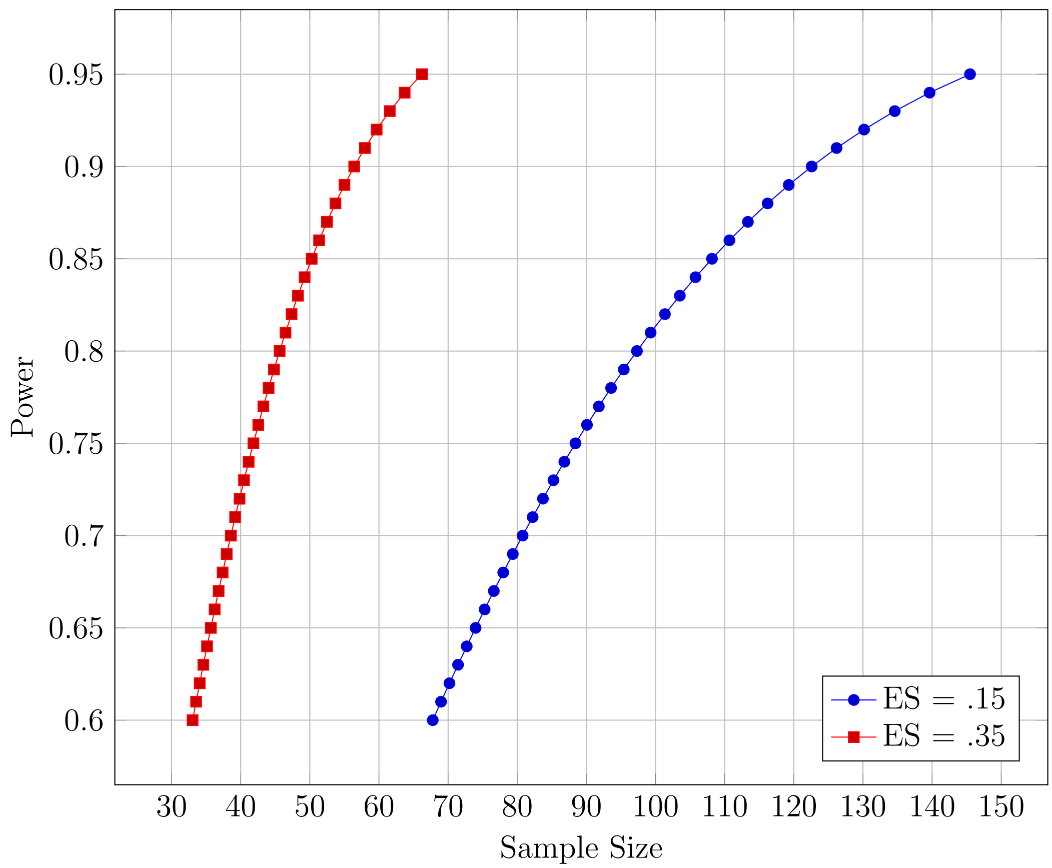


Figure G.1: pH Power Graph. The power is shown as a function of pH

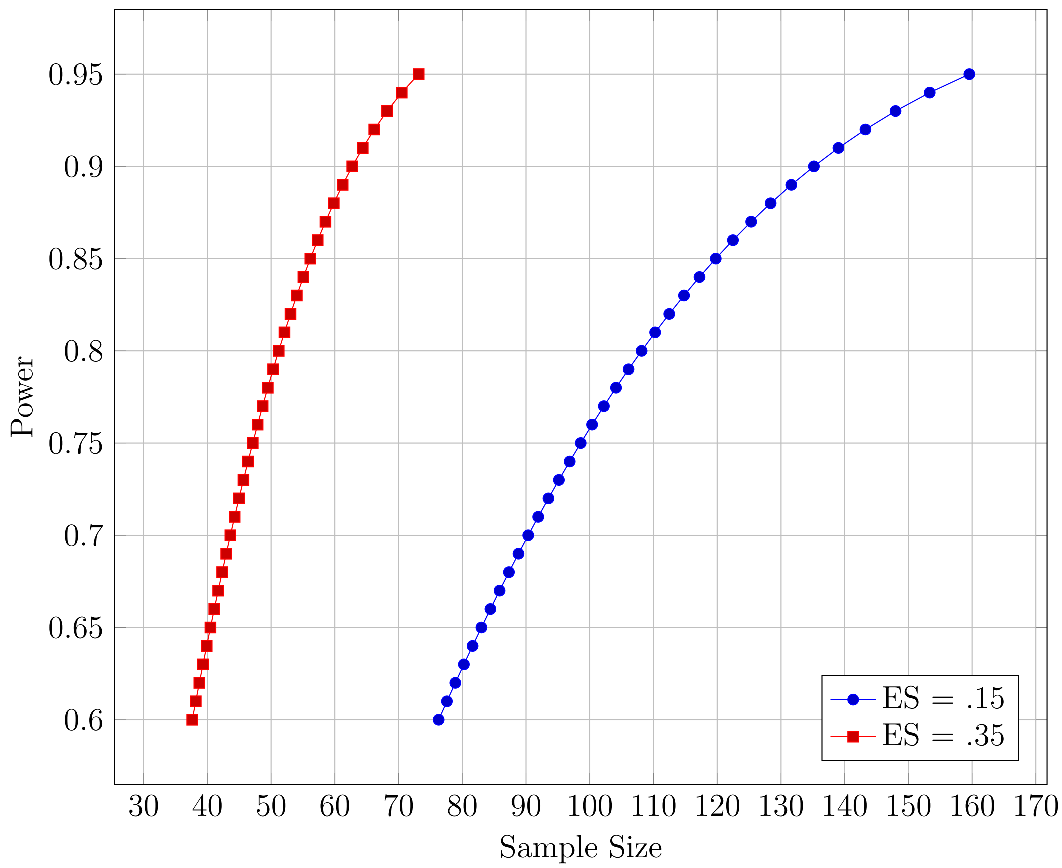


Figure G.2: ANC and Nitrate Power Graphs. The power graphs for ANC and Nitrate are the same because they both have the same number of predictors.

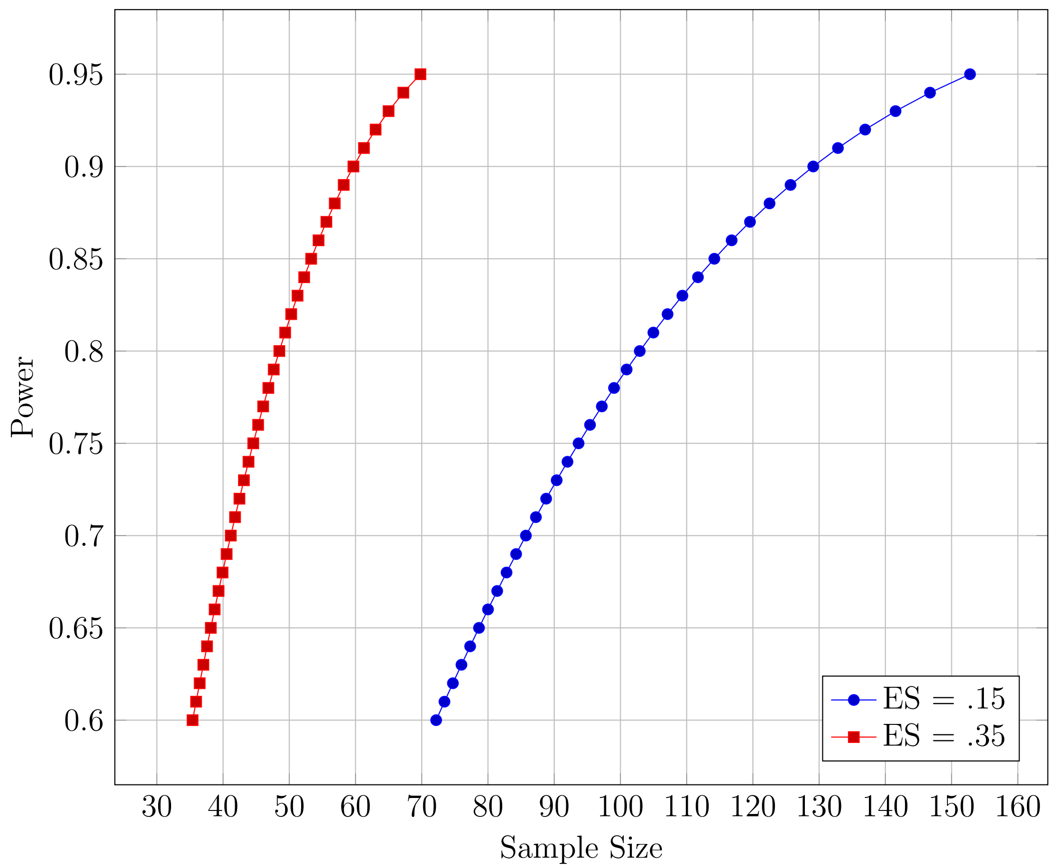


Figure G.3: Sulfate Power Graph

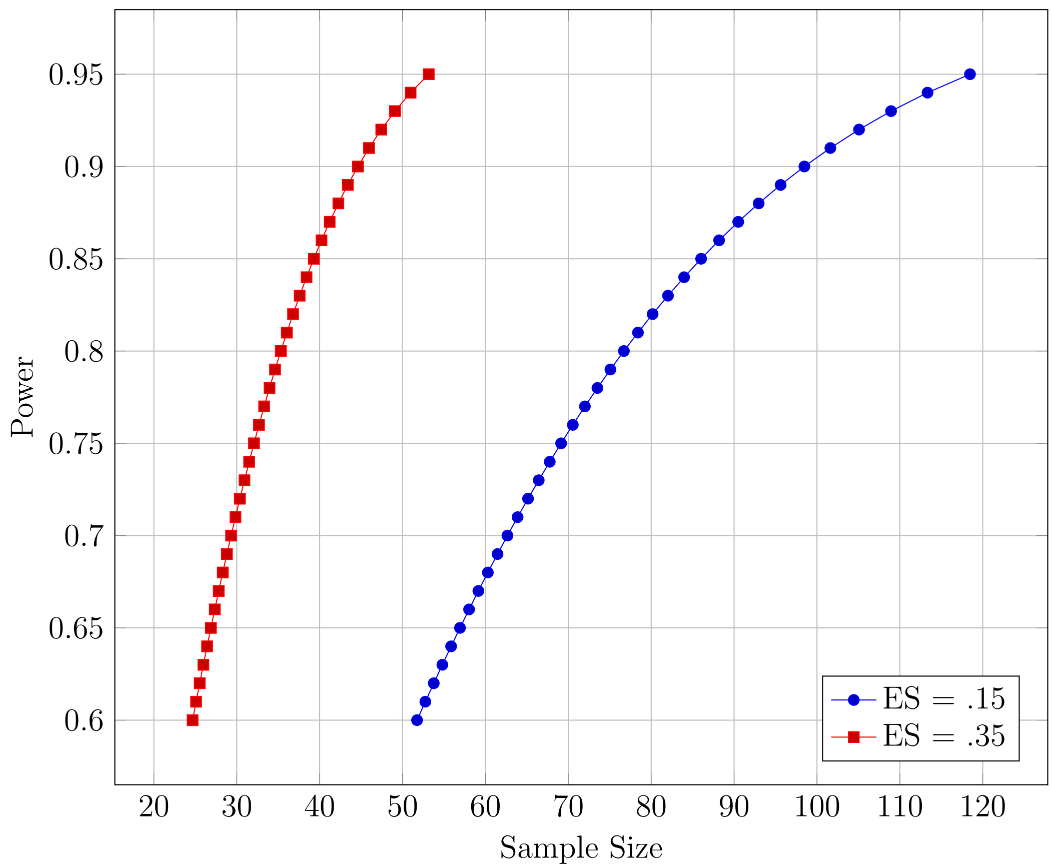


Figure G.4: Time Variables Power Graph

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.