To the Graduate Council:

I am submitting herewith a thesis written by Tim Pobst entitled "Statistical 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.

Dr.John Schwartz, Major Professor

We have read this thesis
and recommend its acceptance:

Dr. Bruce Robinson

Dr. Qiang He

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

To the Graduate Council:

I am submitting herewith a thesis written by Tim Pobst entitled "Statistical Analyses on Legacy Data for the GRSM Stream Survey." I have examined the final electronic 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.

Dr.John Schwartz, Major Professor

We have read this thesis
and recommend its acceptance:

Dr. Bruce Robinson

Dr. Qiang He

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

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

Statistical 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

dedication...

Acknowledgements

I would like to thank... Dr. Schwartz, Keil Neff, Matt, and Steve Moore.

I would like to thank all the faculty and staff in the civil and environmental engineering program. I was never lacking in offered help, from Larry and Ken to the Professors and the secretaries.

I would like to thank Dr.Schwartz for giving me the opportunity for a graduate degree. My responsibilities involved a lot of field work in the Great Smokey Mountains and I never bored of bragging about it.

I would like to thank Matt Kulp and Steve Moore of wildlife and fisheries in the GRSM for funding me and any work done in the park.

I would like to thank Mei Cai and Keil Neff who were post-docs for much of the time I was working on my degree. Sometimes it was like having multiple bosses saying different things at once but most of time it was multiple mentors that could help me if one was unavailable.

I would like to thank Chris Rollison and Keil Neff for teaching me everything I need to know to help on the GRSM projects.

I would like to thank Jordan Hayes and Matt Aplin who were the two primary undergraduate helpers regarding GRSM work.

Some quotation...

Abstract

Abstract text goes here...

Contents

List of Tables

List of Figures

Chapter 1

Introduction

Text and tables should show up.

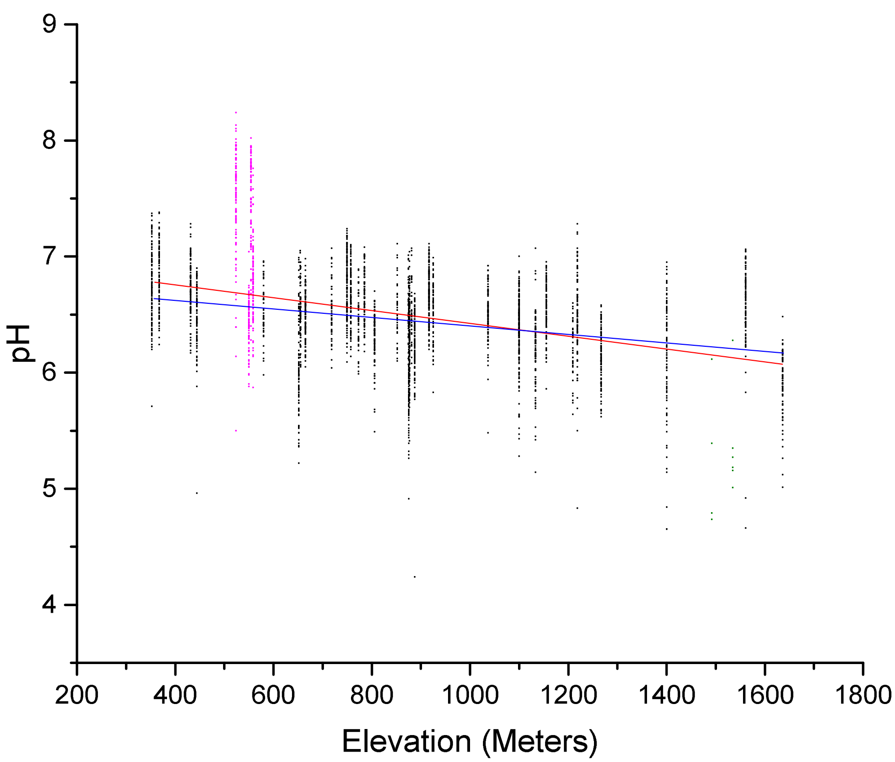


Figure 1.1: pH plotted vs. Elevation. With and without outliers.

Acid rain is believed to negatively affect The Great Smokey Mountain National Park

Acid Deposition, more commonly known as Acid Rain, is a constant problem for the i

Acid Deposition occurs when the emissions of sulfur oxides (SOx), and nitrogen oxi

Acid deposition greatly impacts surface water and the surrounding environment. The

Acidification of bodies of water can be either chronic or episodic. Chronic acidif

The Great Smoky Mountains National Park (GRSM) is located in the southern Appalach

In order to monitor acid deposition the park has a program called the Inventory an

Figure 1-1

This figure shows all pH data from 1993 to 2012 vs. Elevation (m). The red trend

Figure 1 is a graph of all measured pH values for Stream Survey between the years

In support of GRSM natural resource management, stream water quality has been moni

Table 1 shows the current historical elevation classes with the number of sites th

The National Park Service is currently developing a Vital Sign Monitoring Program

Objectives of this study were to:

\begin{itemize}

\item characterize time trends in stream pH and acidic anions among elevation ran

\item characterize sampling variance based on available water quality data, within

\end{itemize}

\begin{itemize}

\item Has stream pH and acid anion concentrations changed among three time periods

\begin{itemize}

\item ANOVA

\item Time trends

\end{itemize}

\item What is the statistical power for water quality parameters based on frequenc

```
\begin{itemize}
\item Post Hoc Analysis
\item A Priori Analysis
\end{itemize}
\end{itemize}
The thesis is organized into two separate chapters following the two above researc
```

1.1 Stream Health Indicators

The stream survey includes six stream systems and five of them are collected every two months and analyzed in a lab for many water quality variables including pH, ANC, NO_3^-, SO_4^{2-} and some metals. The stream survey water quality data includes measurements for pH, ANC, conductivity, acid anions (CL^-,SO_4^{2-},NO_3^-, ammonia (NH_4^+), the base cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+), 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

Instruments

Chapter 2

Trend Analysis

The quality of water in the GRSM is an ongoing concern for the park, as the acidification of the streams can have significant negative effects on wildlife and vegetation. In order to support their mission of monitoring the water quality of the GRSM, a stream survey program collects water samples from all over the park. These samples are then analyzed for indicators of the health of the water, while trying to predict where the water quality is headed in the future. A brief introduction to trend analysis is provided in section 2.1. The methods utilized for trend analysis will be detailed in section 2.2, with application of these methods in section 2.4.

2.1 Introduction

In order to ascertain whether the water quality is increase on decreasing in the GRSM, a temporal trend analysis is necessary in which the water quality data is analyzed for possible trends. Several authors have previously published work in this area. Robinson et al. (2008) completed a trend analysis on the stream survey data in 2002 using step-wise multiple linear regression in order to determine if time was a significant predictor of pH, ANC, sulfate, or nitrate and found that between 74 % to 24% of the data could be explained by the four predictors. This was repeated again in (Meijun Cai, 2012).

Linear regression, in which an independent variable is modeled by a predictor variable, assume that the independent variable can be modeled as a linear combination of the a predictor variable to a normally distributed random error term. Multiple linear regression extends linear regression to express a single predictor variable as a linear combination of a vector of independent variables with a matrix of coefficients and a vector of error terms. Given a vector of time series indicators of stream health, $\overrightarrow{x(t)} = \left\langle ANC(t), SO_4^{2+}(t), \cdots \right\rangle$, a linear regression model of independent variable $\overrightarrow{\mathrm{pH}(t)}$ can then be expressed as (2.1), where β is a matrix of regression coefficients to within an error term ϵ.

$$\overrightarrow{\mathrm{pH}(t)} = \overrightarrow{x(t)}^{\top}\beta + \epsilon(t) \tag{2.1}$$

Linear regression models assume that the variance of each predictor is constant, and the predictor vectors are independent. These conditions are satisfied in the modeling of stream water quality due to **CAN YOU JUSTIFY THE ASSUMPTIONS?**.

Multiple linear regression models often have an excessive amount of predictor variables, some of which do not have an impact on the model. Step-wise multiple linear regression is a semi-automated process of building a statically valid model by successively adding or removing variables based on the t-statistics. Generally, this involves a forward selection criteria in which variables are added to the model if they provide a statistical improvement to the model, and a backwards selection in which variables that have been added but are no longer statistically meaningful due to the addition of other variables are removed. Several statistical packages are then available which automate this process.

2.2 Methods

A general, stepwise multiple linear regression is then applied to the stream water quality in the Smokies.

In order to avoid the tendency of linear regression to over predict the data the complete data set was divided into smaller subsets. It is expected that different elevation bands will require different regression coefficient matrices due to the differences in geology that accompany the elevation bands because upper elevations are more effected by acid rain (Weathers et al., 2006). **Isn't this a chicken and the egg problem? The acid rain has greater effect because of the geometry** Upper elevation sites also need to be sampled at a higher rate in order to ensure that the data in the band is statistically sound (Weathers et al., 2006). Previous researchers used an artificial clustering in 500 meter increments, while elsewhere in this work (**??**) a statically relevant clustering. However, this attempt was futile, so a banded artificial clustering was employed.

The elevation classes used in this paper were set up to include a minimum number of sites in order that the upper classes would not be too weak to be useful. These are different from the historic eleven elevation bands which were separated by arbitrary 500 foot intervals. Some of the upper bands only contained one site. The more sites you have the closer you get to fully describing the water quality and after years of collection this one site can describe its own features but it cannot describe characteristics of the elevation band very well. The divisions are presented here in Table 2.1.

Without adding sites, the best way to do this is to reorganize the elevation bands. Dividing all the data into three different time sets, six elevation bands and studying four different dependents will create 72 different trend lines. Two more factor divisions of the data include dividing the data by elevation classes and four dependent variables (pH, ANC, NO_3^-, and SO_4^{2-}).

Table 2.1: 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

2.2.1 Reduction of Variance

As shown in Figure 2.1 there is significant variation of the pH with elevation. The trend analysis will use stream survey data from 1993 to 2012 using the statistical programs JMP and SPSS for analysis.

Twenty years of data were available for this paper from the years 1993 to 2012. A single trend line containing all 20 years is unrealistic because it will not show why there is a difference in the previous trend analyses or if there was a change in trend after 2008. The opposite trends reported in Robinson et al. (2008) and Meijun Cai (2012) 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 sectioned off from 1993 to 2002 to equal the years analyzed in Robinson et al. (2008). A third data set will be created 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.

All of the statistical analysis was completed in statistical software. Initial data smoothing and influential data points were found using JMP 9. A power analysis was

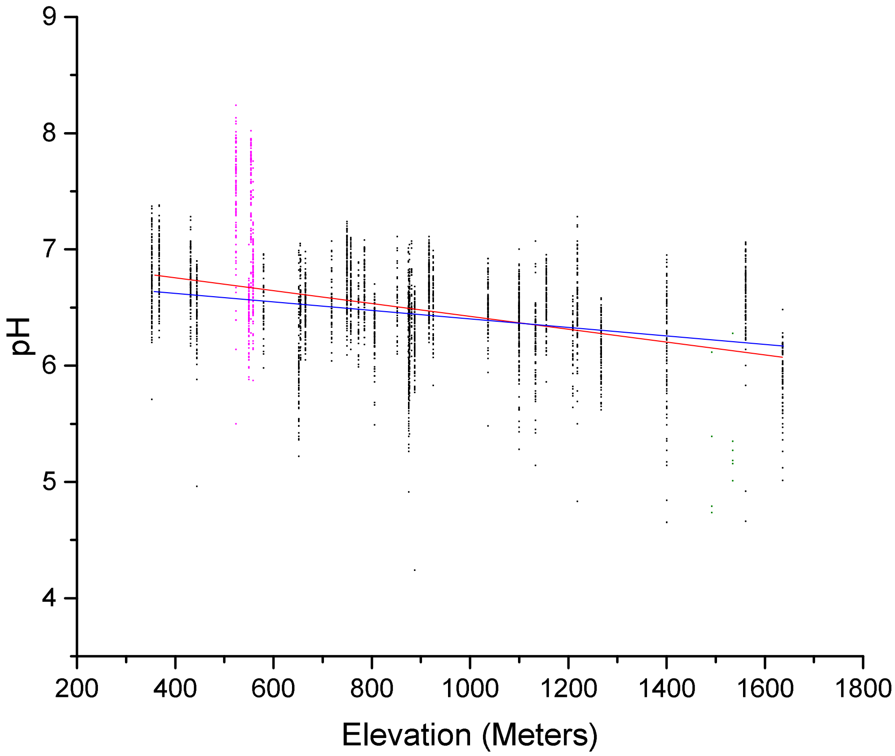


Figure 2.1: pH plotted vs. Elevation. With and without outliers.

performed using G*power, and all other statistical analyses were performed using SPSS.

Several plots were created in order to reduce the variance of the data before any statistical analysis was attempted. JMP was chosen for this task based on its ease of use in plotting data. A plot of pH vs. time is shown in Figure 2.2 for **NUMBER of SITES** from 1993 to 2012. Figure 2.1 shows the pH vs. elevation plot. It shows 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. pH was plotted against the month that the sample was collected to check for

Figure 2.2: Temporal trend of pH data for a variety of stream sites. Note that there is an inflection around **date**.

seasonality. Seasonality was expected and found for pH over one year. The variance caused by seasonality will be removed with sine and cosine functions.

Much of the variance in Figure 2.1 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). 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. Site numbers 237 and 252 are sites which are down hill of road cuts that have exposed the underlying anakeesta formation to runoff. 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.

Stormflow is both influential and detrimental to GRSM water quality. Storms can bring high intensity rain fall which can very quickly reduce the pH and ANC of streams. In streams with low ANC and pH, episodic stream acidification can be harmful to aquatic life (Neff et al., 2009). Stormflow runoff can have a higher contribution to stream acidification than baseflow because it transports protons left in the upper layers of the soil by acid deposition. Stream acidification caused by stormflow can cause base cation exchange through the leaching of the surrounding soil. When the inherent base cation minerals run out, excess H^+ and Al will be released into the water. Increasing the H^+ concentration will lower the pH, and Al is toxic to biotics. Healthy streams can rebound to normal pH values; unhealthy streams can have permanently lowered ANC due to leaching. 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 (2012). Water quality data after 2010 had not been characterized. If all stormflow observations are to be kept in the data, 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.

The regression process includes preparing the data and identifying influential observations. The output of a step-wise regression analysis performed in SPSS can be configured to complete many different analyses in order to smooth the data. 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 the analysis was re-run and more influential observations could be found, and attention would need be given to these also. This process was completed for all four of the dependent variables, (pH , ANC, NO_3^-, and SO_4^{2-}).

The step-wise variable selection process requires a list of variables to choose from. These variables are reported in Table C.1. The variables chosen for this list were chosen from those chemistry values recorded in the full stream survey dataset. One benefit of choosing only variables directly from the stream survey dataset is a high ease of repeatability for the future. The step-wise process regulates entry into the equations by the probability of the F statistic. If this statistic were between .05 and .10 then the variable could stay. The variables selected were used to create the fixed models presented in Table 2.2. 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^{+} measurements. 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 $\log_2(BC)$.

Table 2.2: 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

The difficulty in modeling a time trend is the high amount of variation within the datasets. While trying to determine a time trend other variables are added besides those that explain a trend in time. 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.

Elevation was not a significant predictor for any of the dependent water quality variables chosen. The dependent variables were regressed using simple linear regression against elevation in meters in order to determine their trends by elevation. These trends encompass all elevations; no elevation bands were used.

2.3 Results

Julian date coefficients are are reported in Robinson et al. (2008) for each of the eleven historic elevation classes and across each of the dependent variables (pH, ANC, NO_3^-, and SO_4^{2-}). Julian date coefficients for this paper were reported in similar tables. 144 different Julian date coefficients were calculated and are presented in two tables. Table D.1 records the Julian date coefficients calculated using the equations in Table 2.2 and Table 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.

2 of the 72 trend lines in Table D.1 are insignificant. In contrast 50 of the 72 trend lines in Table D.2 are insignificant. Setting the linear regression α at .05 forces any trend with a p-value greater than .05 to be insignificant. Insignificance rejects the hypothesis that β(the coefficient) $\neq 0$. A p-value greater than .05 means that there is greater than a 5% chance that $\beta = 0$ or in this case the Julian date coefficient =0.

2.3.1 Step-wise Julian date coefficients

pH

The Julian date coefficients in Table D.1 for pH showed negative time trends in three statistically significant regression lines, all in the time range of 1993-2002. These lines were in elevation classes 2, 3, and 5. There is one degrading trend in the third time set (2009-2012) and in the fifth elevation class but it is insignificant. Most of the trend lines report that pH is increasing over time.

ANC

Trends for ANC fluctuate while evaluating across time sets and elevation classes . 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 degrading trends in set 2 becomes positive in set 3. When comparing time set 2 to set 3, ANC trends are growing over time.

Nitrate

NO_3^- trends in set 2 are all positive. In set 3 NO_3^- has a decreasing trend in elevation class 4. The NO_3^- trends for set 1 are half positive and half negative. But from the years 2003 to 2008 all of the NO_3^- trends are positive. In set 3, the trend in elevation class 4 has a negative trend.

Sulfate

SO_4^{2-} has mixed positive and negative trends for set 1 but all positive trends for set 2. Half of the SO_4^{2-} trends in set 3 are negative (1, 3, and 6).

2.3.2 Julian date coefficients from time variables only

In Table D.2 only 20 of the 72 regression lines are significant, those that have acceptable p-values less than .05.

pH

The dependent variable pH in set 1 has zero significant lines, set 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 Table D.1.

ANC

There are only two significant regression lines in for ANC in Table D.2. Elevation class 5 in set 1 has a decreasing trend at -.148, there are no significant lines in set 2 and set 3 elevation class 5 has a positive trend at .891.

Nitrate and Sulfate

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

2.3.3 Elevation trends

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. Every value in the right most column decreases for the water quality dependents as the table moves forward in time sets except for the base cations .

2.3.4 Results by Comparison

In comparing table 4 from Robinson et al. (2008) with Table D.1 from this study, it needs to be noted that the elevation classes are different and the data sets have slightly changed throughout the years. The largest difference is the reduction of 90 sites to 43. Abrams was not included in this analysis but was included in Robinson et al. (2008). This difference could explain the differences seen in the old elevation

Table 2.3: 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

classes from Robinson et al. (2008) of 1,2, and 3 and elevation class 1 in this study. Two sites (237, 252) that are in the new elevation class 6 were left out of the statistical analysis as influential observations. These correspond to historic elevation class 9.

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 for set 1 for pH found in this study were negative in Table D.1. All of the rest of the pH trends for Julian date for both trend analyses are positive when they are significant.

pH and ANC For a data set of 92 sites within the time frame of 1993 to 2009 Meijun Cai (2012) 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. These values are close to those found in this study for the years of 2009-2012, but the slopes in set

1 and 2 are much steeper. In set 3, pH is significantly lower with a trend of -.0286 pH units per 1000-m gain and ANC is a little bit lower with a trend of -35.689 μeq L^{-1} per 1000-m gain(Table 2.3).

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 2.3 and then by 6 μeq L^{-1} between set 2 and 3. In contrast, an insignificant negative trend with elevation was found in Meijun Cai (2012) for the years 1993 to 2009. NO_3^- follows a similar pattern as SO_4^{2-} in Table 2.3 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.

2.4 Discussion

It is interesting that the step-wise process did not choose elevation as an independent variable for any of the dependent variables. Figure 2.1 clearly shows a decreasing trend for pH while increasing the elevation. Individual elevation classes might be to small to show a significant elevation trend. Increasing acidification with increased elevation was observed in Meijun Cai (2012) will analyzing the entire 1993 to 2009 dataset available. This suggests that there is an elevation trend it is just not as important as other factors when studying acidification in the GRSM.

A trend in time is also clearly evident with a simple plot of pH vs. time but the mostly insignificant trends of Table D.2 suggest otherwise. The three time variables alone are not enough to explain the dependent variables. Robinson et al. (2008) found that pH was decreasing over time when looking at stream survey data between 1993 to 2002, although this study found that most of the trends in that period are negative, the trends for 2009 to 2012 are all positive as well as the trends for 2003 to 2008. This is in agreement with values reported in Meijun Cai (2012). The differences between the results in Robinson et al. (2008) and those in Table D.1 and Table D.2 imply that water quality is worse in the past but is getting better. Both Robinson et al. (2008) and Meijun Cai (2012) used more than double the sites of this study and Robinson et al. (2008) allowed Abrams to stay in the data. The differences in the data can account for differences in the results but it is safe to say that water quality in the park is getting healthier.

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, 2012).

SO_4^{2-} has more decreasing trends 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. It is surprising that Meijun Cai (2012) found an insignificant but negative trend in SO_4^{2-} as elevation increases while this study shows only increasing elevation trends for all time sets. When looking at a graph of SO_4^{2-} vs. elevation there are many higher elevation outliers present, these outliers could make the difference in findings.

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 (2012). 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.

The advantage of using regression for trend analysis is its prediction abilities but regression is more difficult than the nonparametric methods of trend analysis. Tests for normality and heteroscedasticity along with variable transformations take care of forcing the usually nonparametric water quality data to be parametric. Nonparametric tests are more robust and do not require as much preparations to run and in the end are more reliable. Robinson et al. (2008) predicted negative trends and 9.4 years for the historic elevation class between 914 and 1067 meters to reach a ph of 6.00. This corresponds exactly to this study's elevation band 4 which received an increasing pH trend in all three time sets. The differences being the sites used and the equations formed through the step-wise process. The equations in Robinson et al. (2008) follow the theory behind acidification much more closely where as the equations created in this study used variables already available in the running stream survey dataset. Prediction is hard and unless it is absolutely necessary to use then the Mann-Kendal test for trends would be much easier, more reliable and more robust (Helsel and Hirsch, 1992).

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.

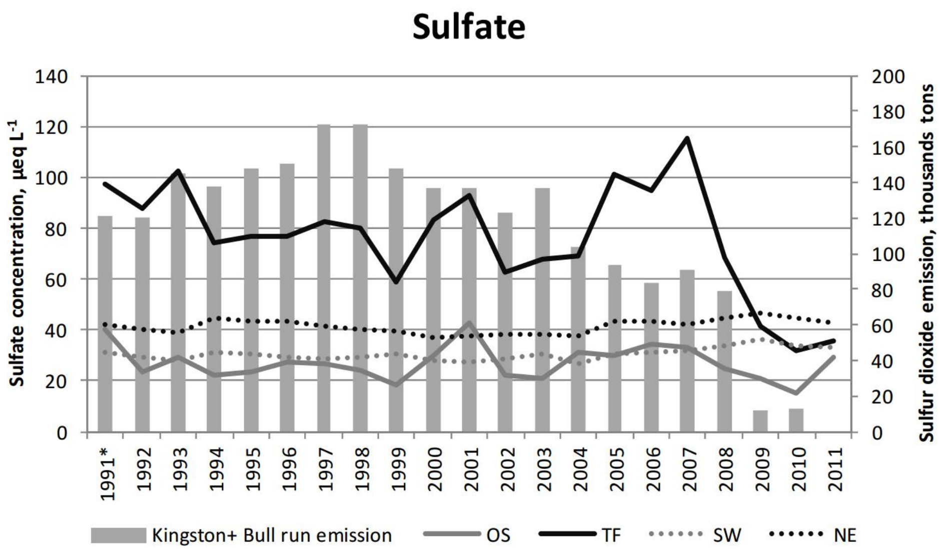


Figure 3.1: Sulfate emmisions of Kingstion and Bull run against those measured in Noland high elevation site.

- 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 (Meijun Cai, 2012)?
  - 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
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

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

- Table 4.2 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.

- Table 4.3 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 Table 4.1 by the current samples per year column in Table 4.3.

- 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!

Bibliography

Bibliography

Cai, M., Schwartz, J. S., Robinson, R. B., Moore, S. E., and Kulp, M. A. (2011). Long-term annual and seasonal patterns of acidic deposition and stream water quality in a great smoky mountains high-elevation watershed. *Water, Air, & Soil Pollution*, 219(1-4):547–562. 18

Cohen, J. (1992). A power primer. *Psychological bulletin*, 112(1):155. 26, 27, 31

Helsel, D. R. and Hirsch, R. M. (1992). *Statistical methods in water resources*, volume 49. Elsevier. 12, 19

Meijun Cai, J. S. S. (2012). Biological effects of stream water quality on aquatic macroinvertebrates and fish communities within great smoky mountains national park. 4, 7, 10, 16, 17, 18, 24

Neff, K. J., Schwartz, J. S., Henry, T. B., Robinson, R. B., Moore, S. E., and Kulp, M. A. (2009). Physiological stress in native southern brook trout during episodic stream acidification in the great smoky mountains national park. *Archives of environmental contamination and toxicology*, 57(2):366–376. 10

Neff, K. J., Schwartz, J. S., Moore, S. E., and Kulp, M. A. (2012). Influence of basin characteristics on baseflow and stormflow chemistry in the great smoky mountains national park, usa. *Hydrological Processes*. 10

Robinson, R. B., Barnett, T. W., Harwell, G. R., Moore, S. E., Kulp, M., and Schwartz, J. S. (2008). ph and acid anion time trends in different elevation ranges in the great smoky mountains national park. *Journal of Environmental Engineering*, 134(9):800–808. 4, 7, 13, 15, 16, 17, 18, 19, 35

UTK (2012). 2011 water quality annual report. Technical report. 20

Weathers, K. C., Simkin, S. M., Lovett, G. M., and Lindberg, S. E. (2006). Empirical modeling of atmospheric deposition in mountainous landscapes. *Ecological Applications*, 16(4):1590–1607. 6, 17

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.

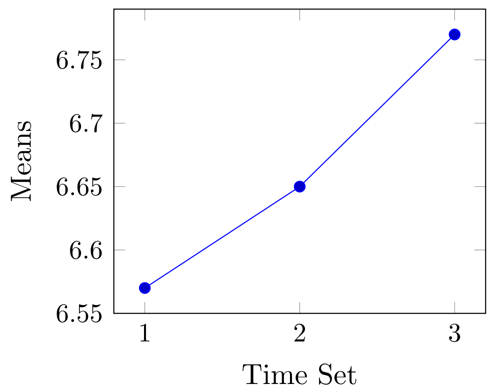
Time set	Elevation class	Elevation range m (ft)	Number of sites	Julian date coefficient, eq/L or pH units (model adjusted r^2) (p-value)			
				pH	ANC	Nitrate	Sulfate
1993-2002	1	304.8-609.6	5	**0.054**	**0.089**	-0.138	-0.190
		(1000-2000)		**0.047**	**0.024**	0.016	0.045
				0.321	**0.106**	0.022	0.001
	2	609.6-762	9	**-0.090**	**-0.060**	**-0.060**	**-0.075**
		(2000-2500)		**0.128**	**0.189**	**0.017**	**0.009**
				0.060	**0.195**	**0.248**	**0.142**
	3	762-914.4	13	**-0.012**	**-0.030**	**-0.048**	**-0.047**
		(2500-3000)		**0.013**	**0.000**	**-0.004**	**-0.004**
				0.817	**0.550**	**0.365**	**0.355**
	4	914.4-1066.8	4	**-0.047**	**-0.151**	**-0.009**	**0.095**
		(3500-3500)		**0.059**	**0.294**	**-0.027**	**-0.016**
				.597	**0.055**	**0.926**	**0.313**
	5	1066.8-1371.6	4	**-0.151**	-0.148	0.330	**0.092**
		(3500-4500)		**0.051**	0.381	0.120	**-0.010**
				.100	0.047	0.006	**0.331**
	6	1371.6<	2	**.156**	**-0.016**	**-0.208**	**-0.036**
		(4500<)		**.096**	**0.075**	**0.092**	**-0.009**
				.092	**0.863**	**0.058**	**0.707**
2003-2008	1	304.8-609.6)	5	.139	**0.009**	0.155	0.192
		(1000-2000		0.040	**0.001**	0.061	0.043
				0.025	**0.888**	0.012	0.002
	2	609.6-762	9	0.145	**-0.090**	0.178	0.138
		(2000-2500)		0.061	**0.081**	0.043	0.014
				0.012	**0.114**	0.002	0.017
	3	762-914.4	13	**0.103**	**-0.006**	**0.047**	**0.099**
		(2500-3000)		**0.020**	**-0.003**	**-0.003**	**0.006**
				0.075	**0.925**	**0.418**	**0.085**
	4	914.4-1066.8	4	0.235	**-0.029**	0.193	0.192
		(3500-3500)		0.148	**0.180**	0.086	0.023
				0.007	**0.728**	0.030	0.035
	5	1066.8-1371.6	4	**0.135**	**-0.112**	**-0.176**	**0.067**
		(3500-4500)		**-0.069**	**0.337**	**-0.082**	**-0.024**
				0.466	**0.443**	**0.401**	**0.701**
	6	1371.6<	2	0.204	**-0.108**	0.236	0.307
		(4500<)		0.081	**0.094**	0.046	0.074
				0.041	**0.274**	0.020	0.002
2009-2012	1	304.8-609.6	5	**0.111**	**0.026**	**-0.036**	**-0.092**
		(1000-2000)		**0.028**	**0.000**	**0.018**	**0.005**
				0.122	**0.718**	**0.619**	**0.207**
	2	609.6-762	9	0.141	**0.017**	**0.020**	**-0.062**
		(2000-2500)		0.052	**0.056**	**0.011**	**-0.010**
				0.037	**0.800**	**0.767**	**0.376**
	3	762-914.4	13	**-0.034**	**-0.027**	**-0.036**	**0.078**
		(2500-3000)		**-0.009**	**-0.002**	**-0.004**	**-0.007**
				0.611	**0.684**	**0.592**	**0.246**
	4	914.4-1066.8	4	0.405	**0.032**	**-0.067**	**-0.129**
		(3500-3500)		0.200	**0.161**	**-0.016**	**-0.011**
				0.000	**0.733**	**0.518**	**0.215**
	5	1066.8-1371.6	4	**-0.031**	0.891	**0.052**	**-0.414**
		(3500-4500)		**0.218**	0.466	**-0.039**	**-0.076**
				0.934	0.007	**0.904**	**0.347**
	6	1371.6<	2	0.264	**0.083**	**-0.021**	**-0.214**
		(4500<)		0.039	**0.058**	**-0.016**	**0.007**
				0.023	**0.462**	**0.859**	**0.068**

Appendix E

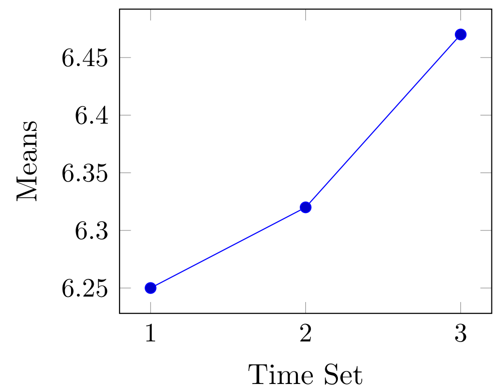
ANOVA/Bonferoni

E.1 pH

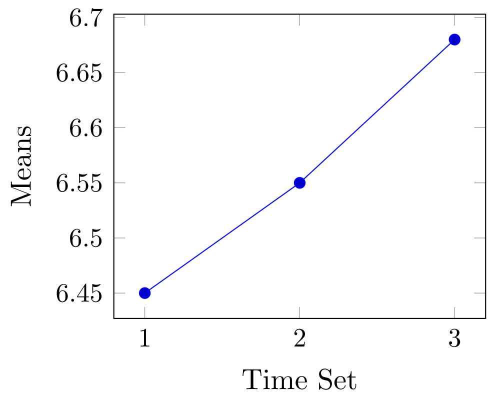
Elevation class 1



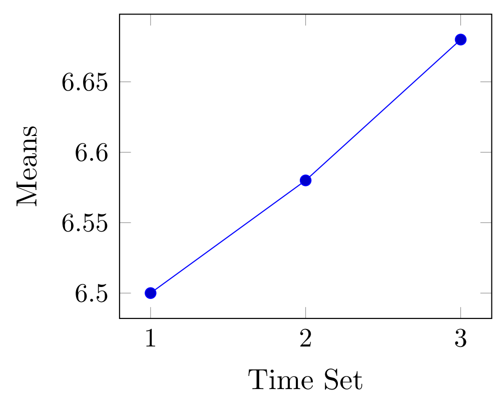
Elevation class 2



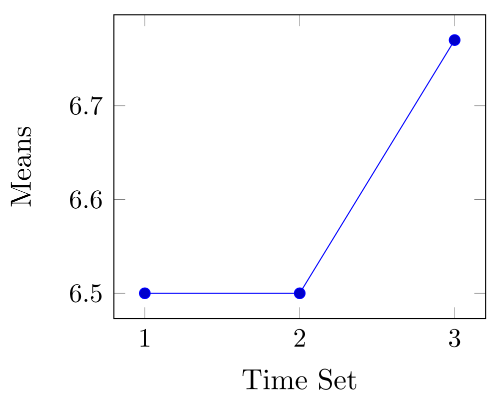
Elevation class 3



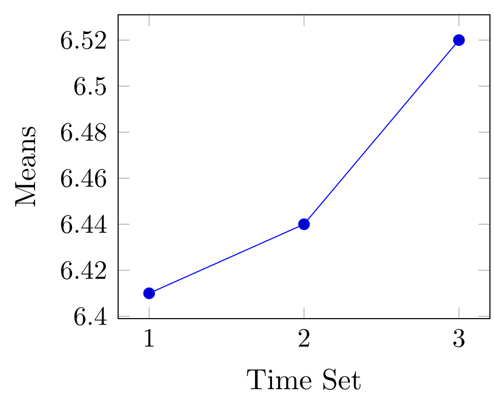
Elevation class 4



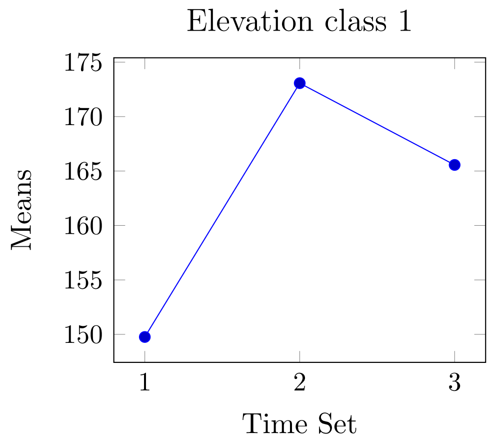
Elevation class 5

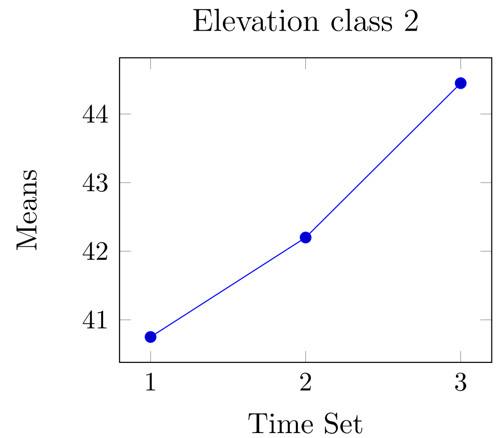


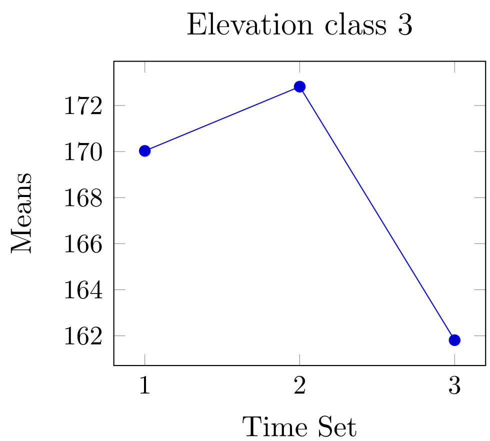
Elevation class 6

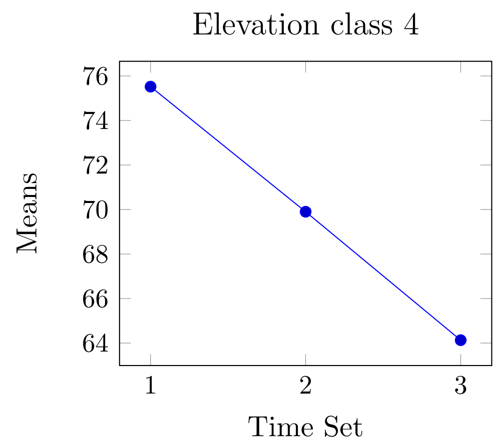


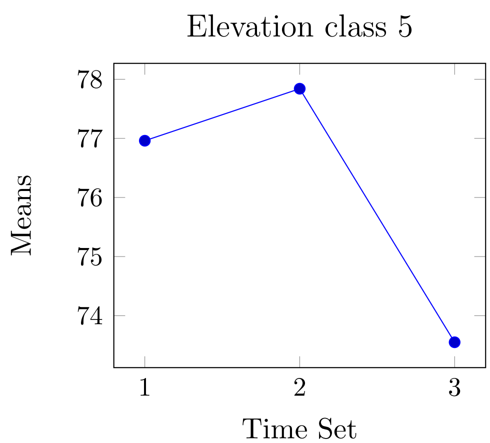
E.2 ANC

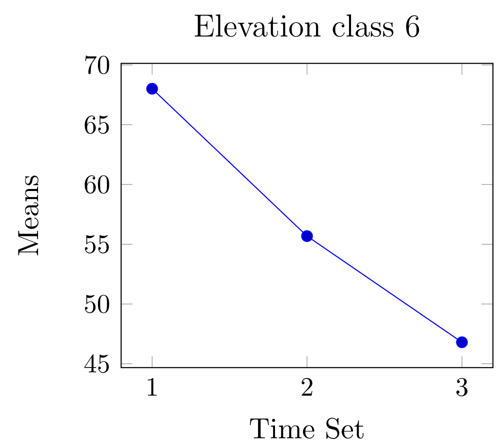

Elevation class 1
Means
175
170
165
160
155
150
1
2
3
Time Set


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

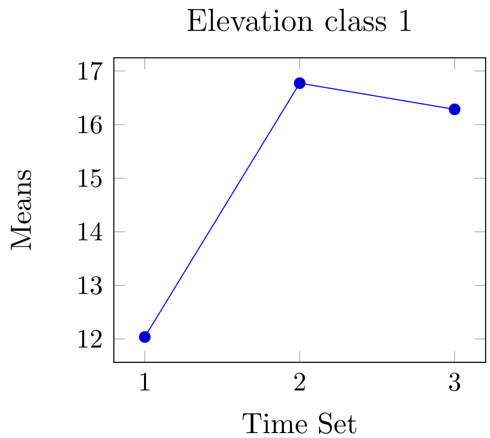

Elevation class 3
Means
172
170
168
166
164
162
1
2
3
Time Set

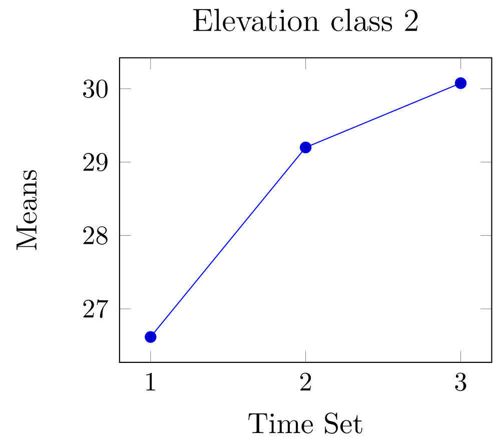

Elevation class 4
Means
76
74
72
70
68
66
64
1
2
3
Time Set

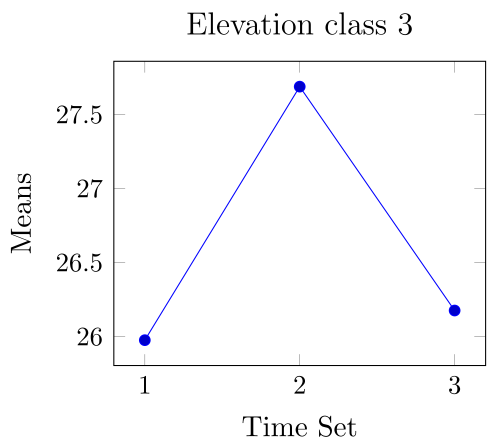

Elevation class 5
Means
78
77
76
75
74
1
2
3
Time Set

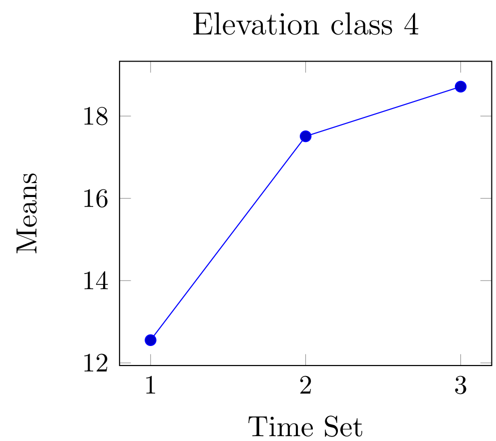

Elevation class 6
Means
70
65
60
55
50
45
1
2
3
Time Set

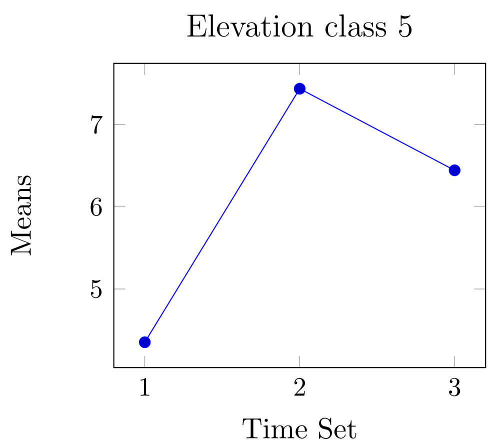
E.3 Nitrate

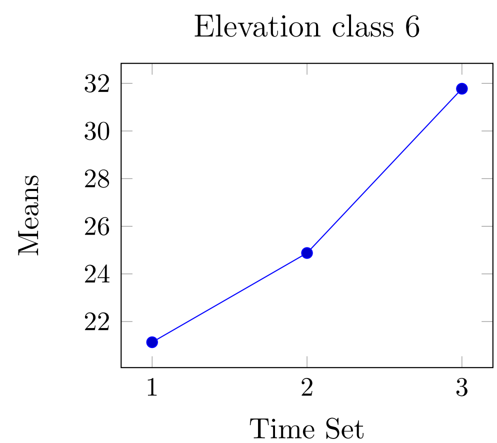

Elevation class 1
Means
17
16
15
14
13
12
1
2
3
Time Set


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

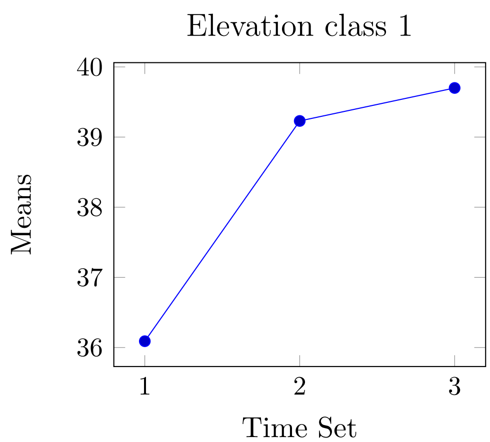

Elevation class 3
Means
27.5
27
26.5
26
1
2
3
Time Set


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

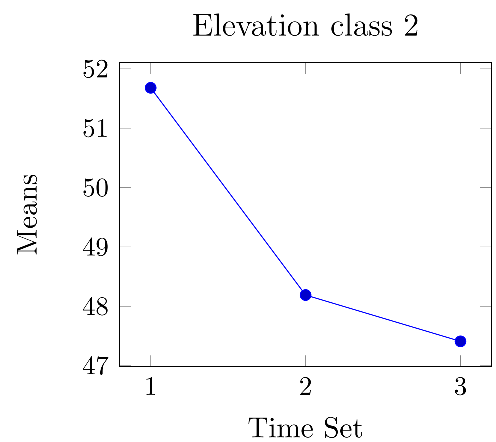

Elevation class 5
Means
7
6
5
1
2
3
Time Set


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

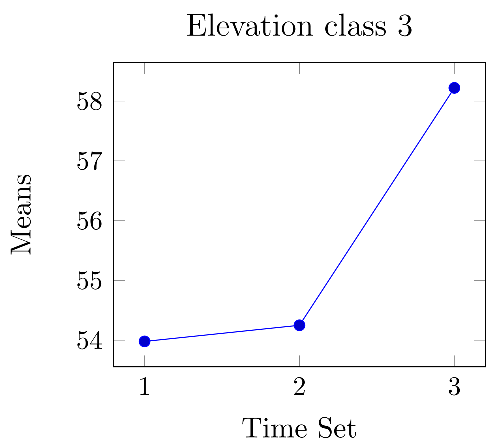
E.4 Sulfate



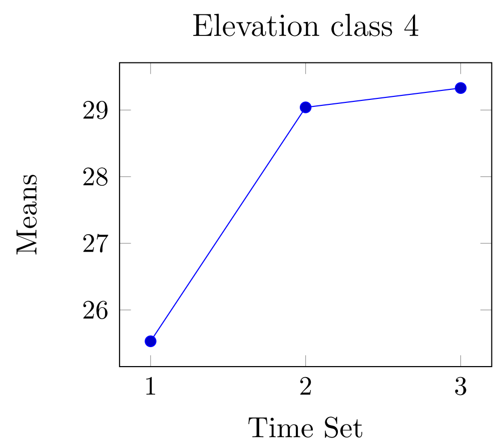
Elevation class 1
Means
40
39
38
37
36
1
2
3
Time Set



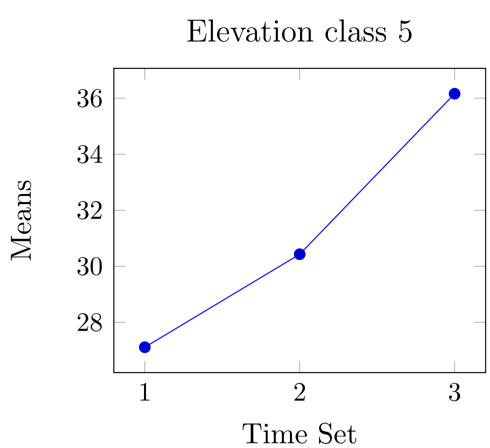
Elevation class 2
Means
52
51
50
49
48
47
1
2
3
Time Set



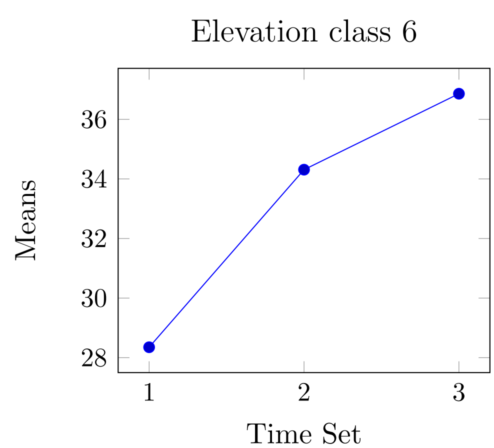
Elevation class 3
Means
58
57
56
55
54
1
2
3
Time Set



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



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



Elevation class 6
Means
36
34
32
30
28
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

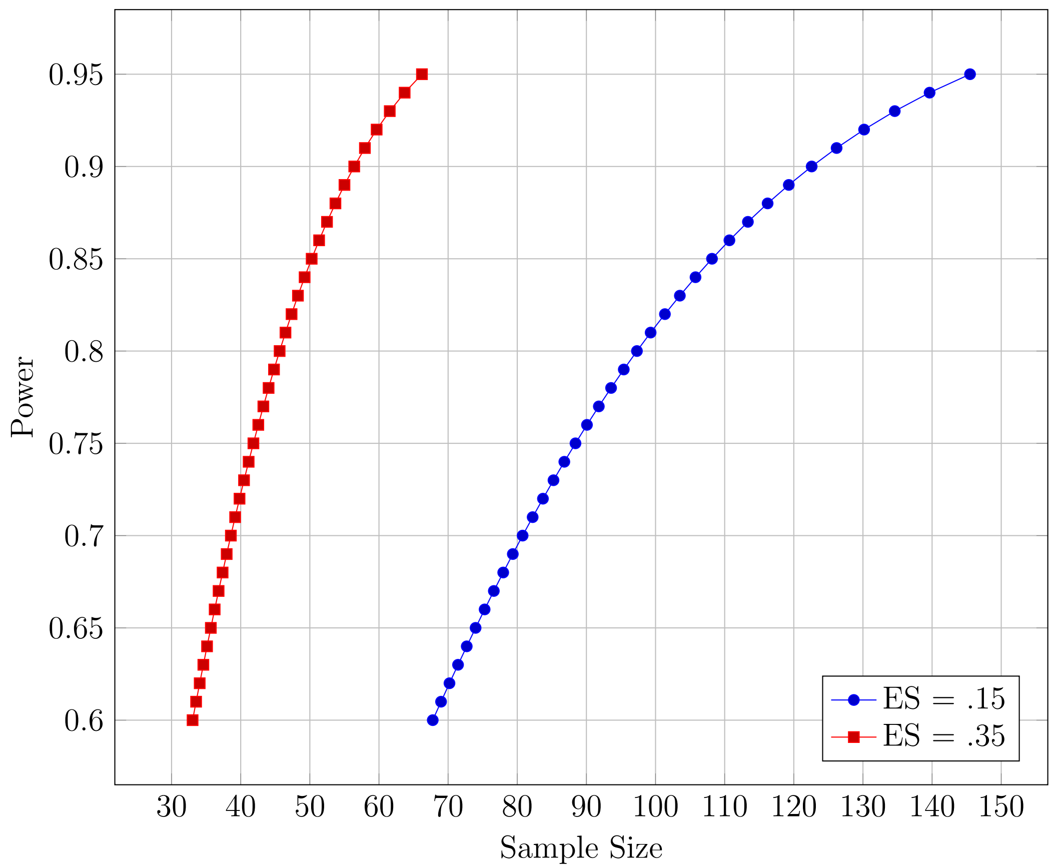


Figure G.1: pH Power Graph. The power is shown as a function of pH

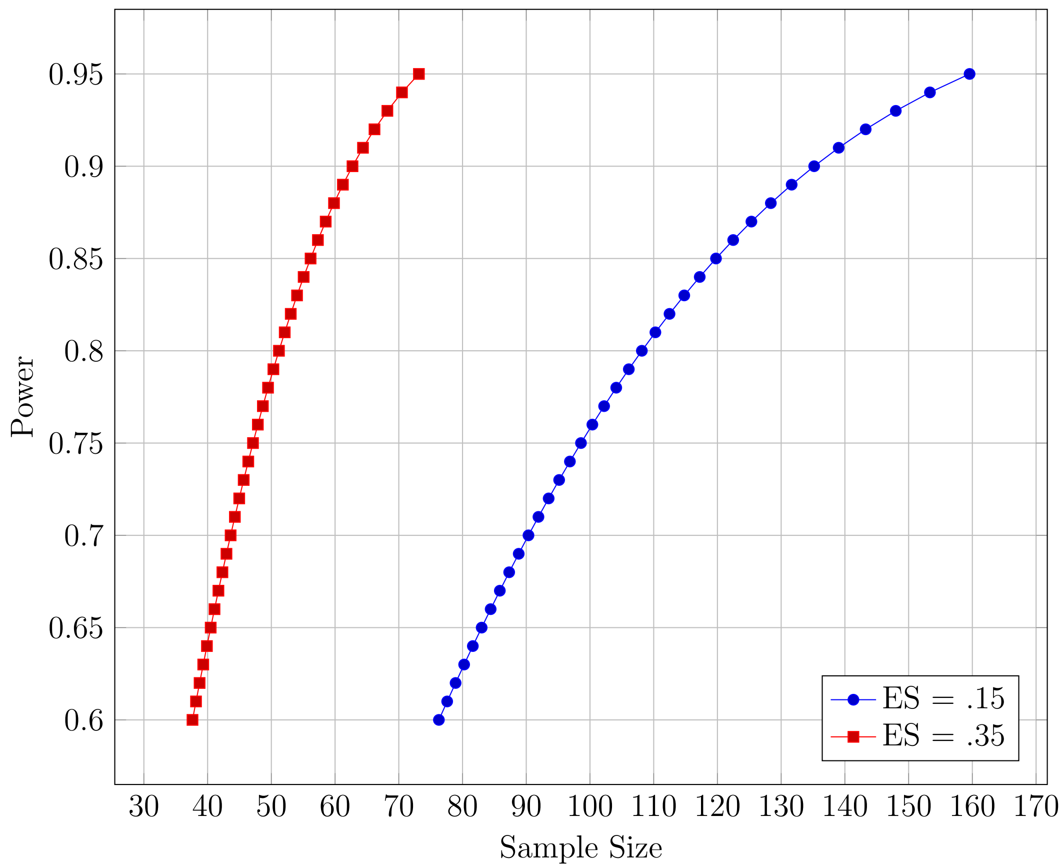


Figure G.2: ANC and Nitrate Power Graphs. The power graphs for ANC and Nitrate are the same because they both have the same number of predictors.

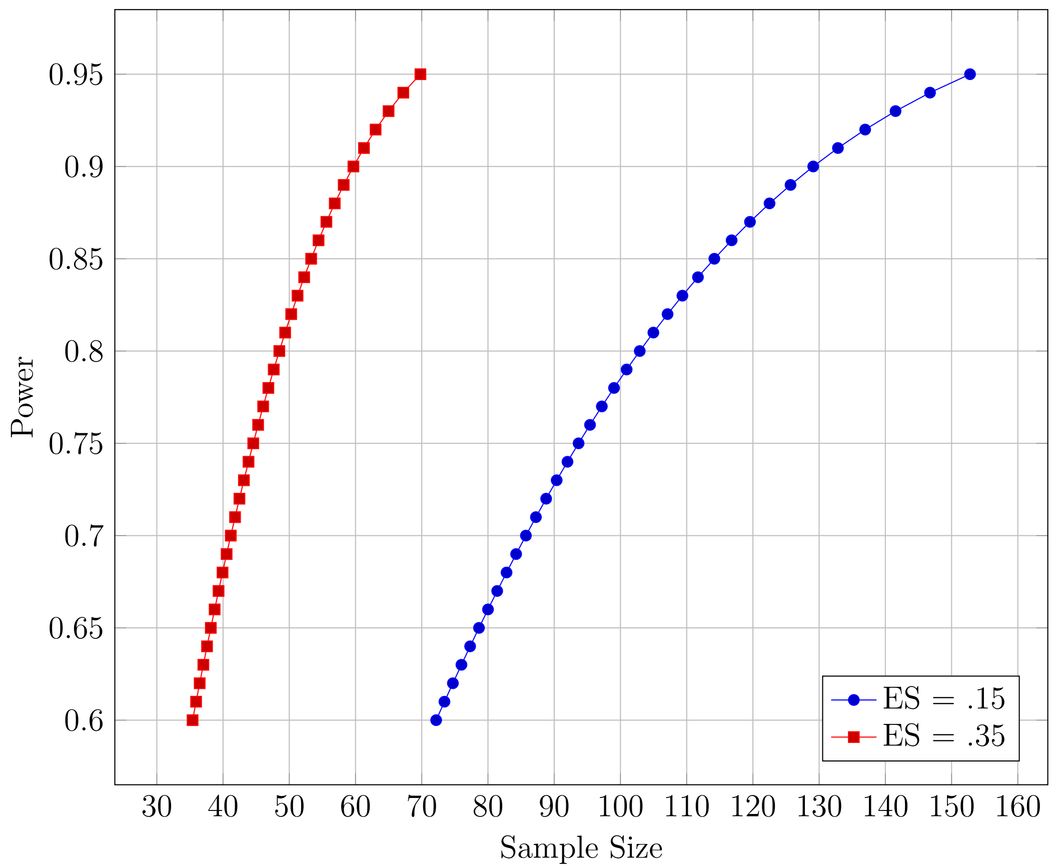


Figure G.3: Sulfate Power Graph

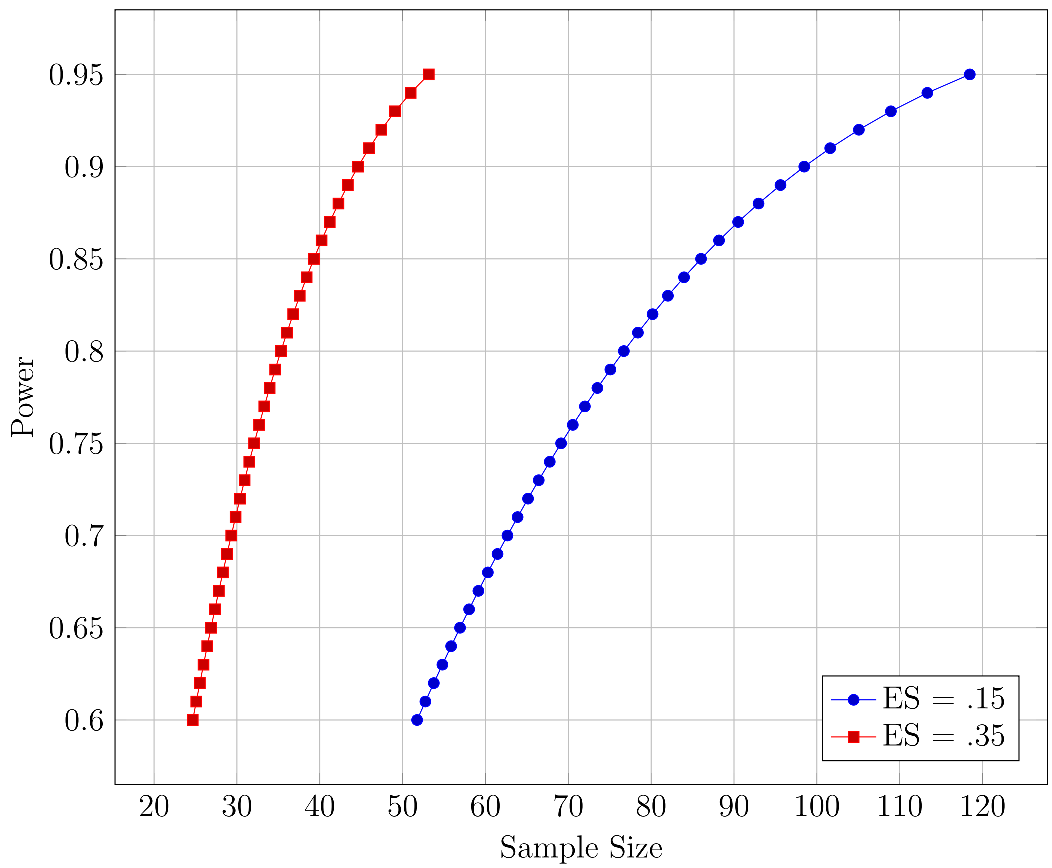


Figure G.4: Time Variables Power Graph

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.