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

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(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

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*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

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# Chapter 1

# Introduction

Text and tables should show up.

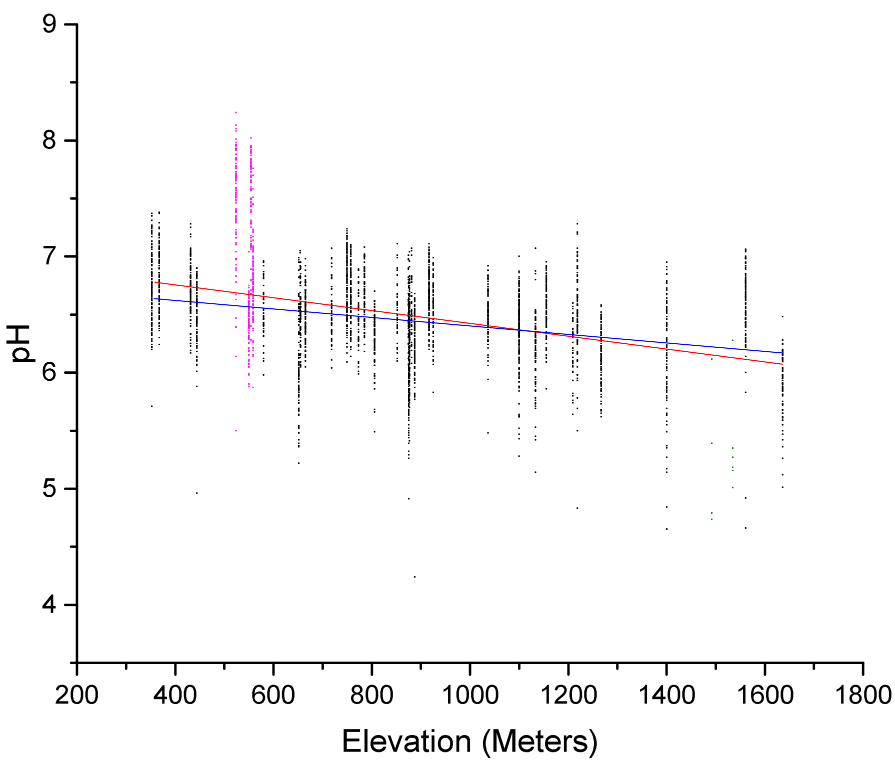


**Figure 1.1:** pH plotted vs. Elevation. With and without outliers.

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

## 1.2 Environmental Factors

There are several environmental factors that contribute to the water quality of the smokies and the mitigation of acid rain. Generally, these are site specific depending upon the geology, and ecology. In addition, sites are also subject to temporal effects including stormflow and seasonal variations.

Stormflow, in which an episodic rain shower deposits an unusually large amount of water in the GRSM, is an influental detriment to GRSM water quality. Storms can bring high intensity rain fall which can 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. Healthy streams can rebound to normal pH values; unhealthy streams can have permanently lowered ANC due to leaching.

The geology of the watershed also impacts the pH of water quality. Sandstone geology, such as the Cases Sandstone, buffers against acid rain very well. This sandstone contributes to high ANC values **why - this should be expanded** which in turn keep the mean pH levels higher than the rest of the sites in the survey. The underlying anakeesta formation also contributes to the watershed water quality. 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. **Again, this section needs to be expanded by another sentence or two What about sites that don't have these?**

**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 $\beta$ is a matrix of regression coefficients to within an error term $\epsilon$.

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

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

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 2.1 for **NUMBER of SITES** from 1993 to 2012. Figure 2.2 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 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 2.2 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


**Figure 2.1:** Temporal trend of pH data for a variety of stream sites. Note that there is an inflection around **date**.

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.

They can be removed on a case by case basis during the regression method.

As shown in Figure 2.2 there is significant variation of the pH with elevation.

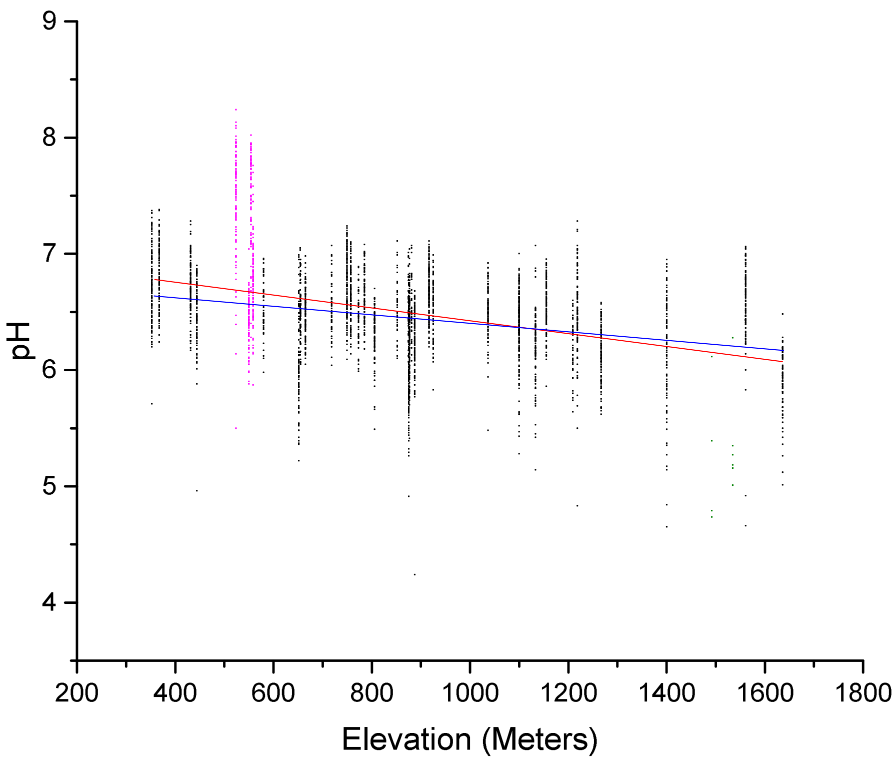


**Figure 2.2:** pH plotted vs. Elevation. With and without outliers.

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.

Measurements taken from stormflow can show uncharacteristically low pH values and high amounts of metals from leaching, as explained in section 1.2. 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.

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 performed using G*power, and all other statistical analyses were performed using SPSS. The trend analysis will use stream survey data from 1993 to 2012 using the statistical programs JMP and SPSS for analysis.

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 $\log_2(BC)$.

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

Table 2.2: Equations created through step-wise variable selection

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

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 $\alpha$ at .05 forces any trend with a p-value greater than .05 to be insignificant. Insignificance rejects the hypothesis that $\beta$(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

**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 |

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 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 $\mu$eq $L^{-1}$ 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 $\mu$eq $L^{-1}$ per 1000-m gain(Table 2.3).

**Nitrate and Sulfate** The positive $SO_4^{2-}$ trends seem to decrease by 2 $\mu$eq $L^{-1}$ between set 1 and set 2 in Table 2.3 and then by 6 $\mu$eq $L^{-1}$ 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 $\mu$eq $L^{-1}$ between set 1 and set 2 and then by almost 5 $\mu$eq $L^{-1}$ 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 2.2 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.

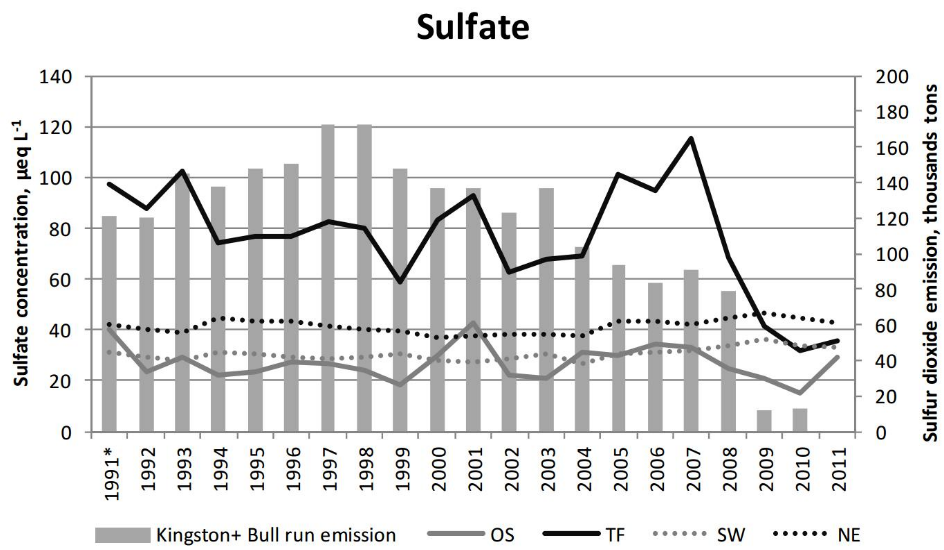


**Figure 3.1:** Sulfate emmisions of Kingstion and Bull run against those measured in Noland high elevation site.

- 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 $\beta$.
- $\beta$ describes failure to reject a false null hypothesis or failure to detect a trend in the data when there really is one.
- $\beta$ is usually described in terms of probability and it's opposite is called power(1-$\beta$)
- 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), $\alpha$(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 $\alpha$ 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!

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# Bibliography


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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 |

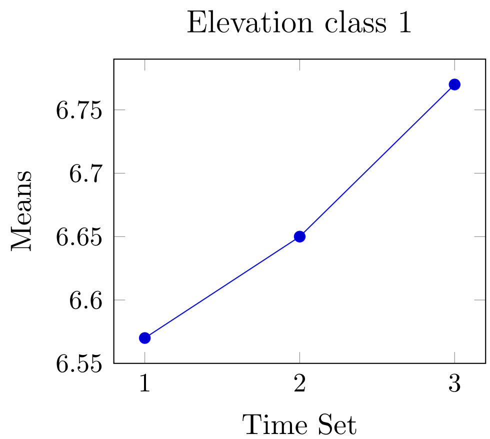
**Table D.2:** Time trend results for specific elevation classes using julian date, cosine($\theta$), and sine($\theta$) only. **Bold** results are insignificant.

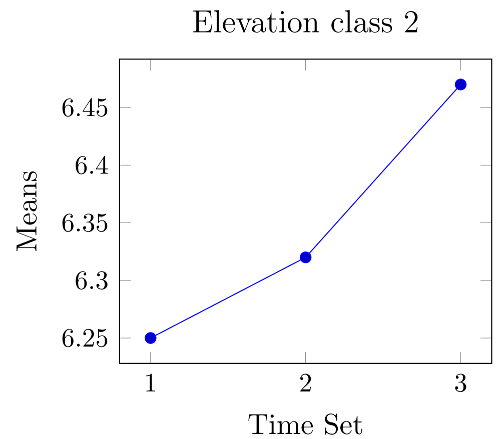
| Time set | Elevation class | Elevation range m (ft) | Number of sites | Julian date coefficient, eq/L or pH units (model adjusted $r^2$) (p-value) | | | |
|---|---|---|---|---|---|---|---|
| | | | | pH | ANC | Nitrate | Sulfate |
| 1993-2002 | 1 | 304.8-609.6 | 5 | **0.054** | **0.089** | -0.138 | -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** |

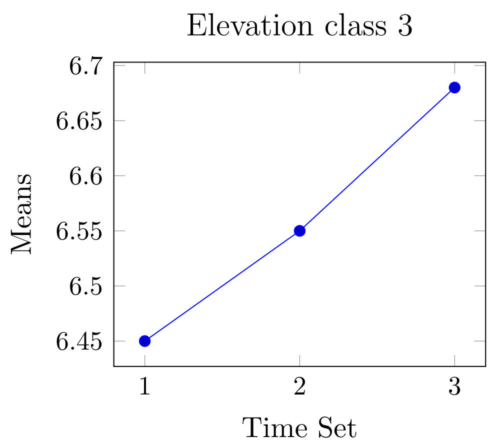
# Appendix E

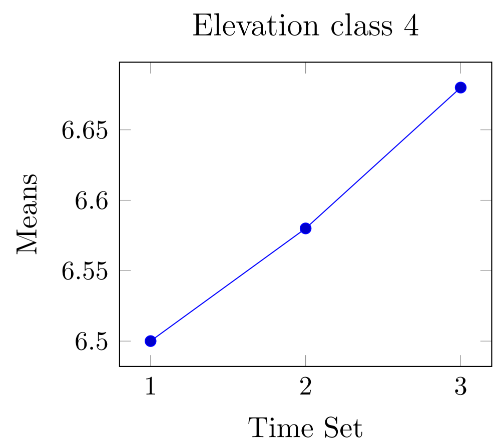
# ANOVA/Bonferoni

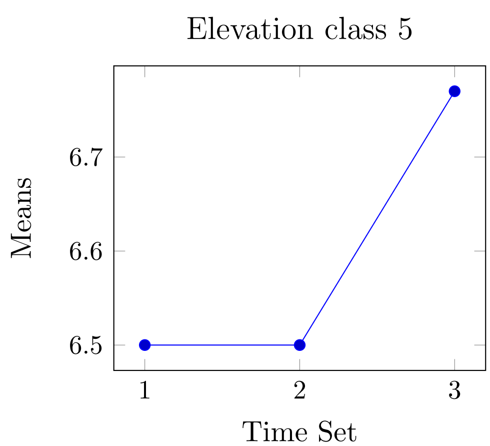
## E.1 pH

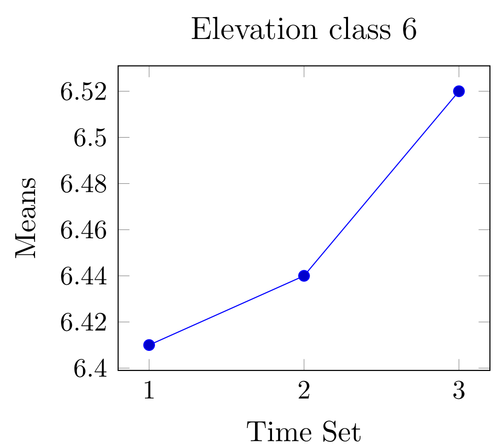

Elevation class 1
Means
6.55
6.6
6.65
6.7
6.75
1
2
3
Time Set


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

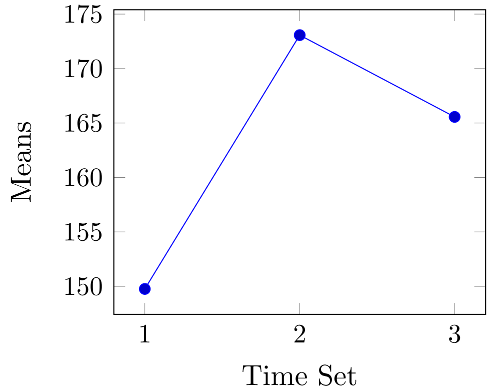

Elevation class 4
Means
6.5
6.55
6.6
6.65
1
2
3
Time Set


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

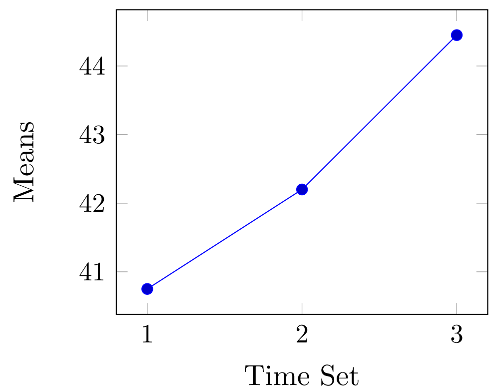

Elevation class 6
Means
6.4
6.42
6.44
6.46
6.48
6.5
6.52
1
2
3
Time Set

## E.2 ANC

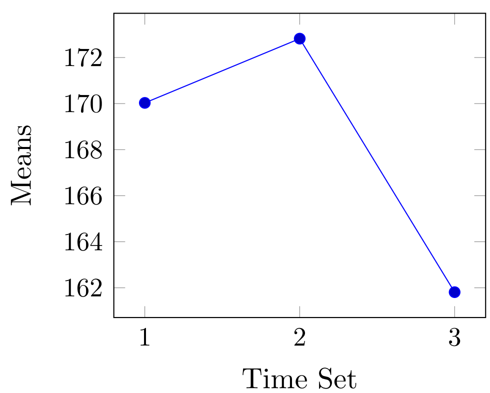
Elevation class 1



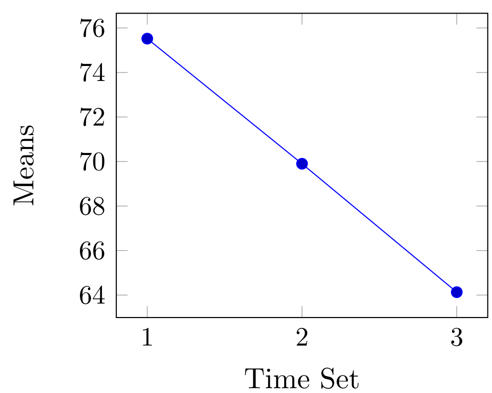

Elevation class 2



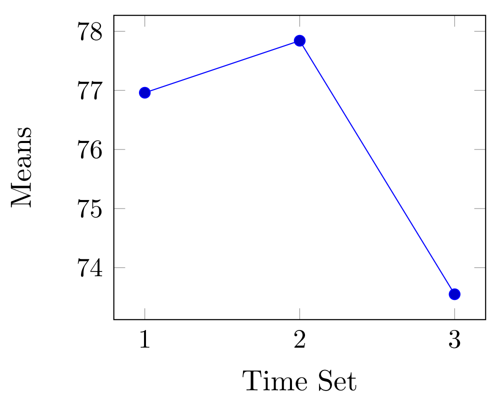

Elevation class 3



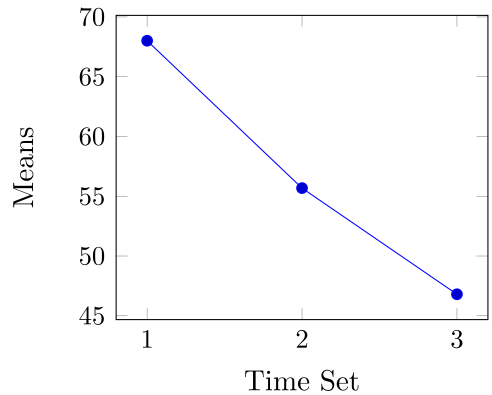

Elevation class 4




Elevation class 5

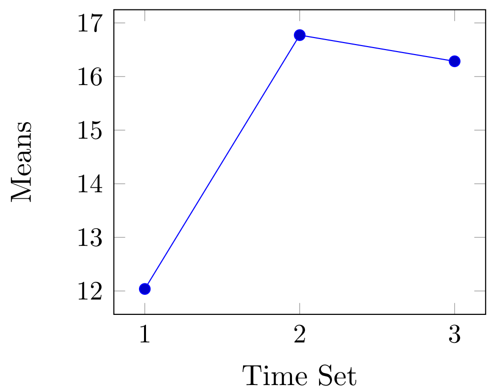



Elevation class 6

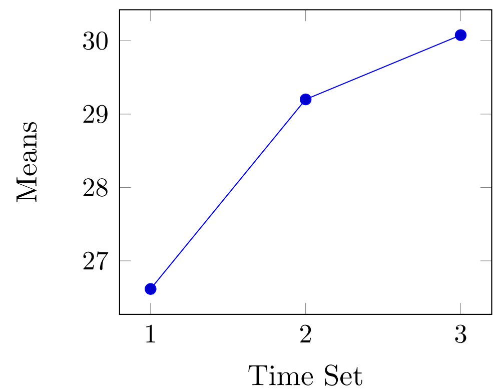


## E.3 Nitrate

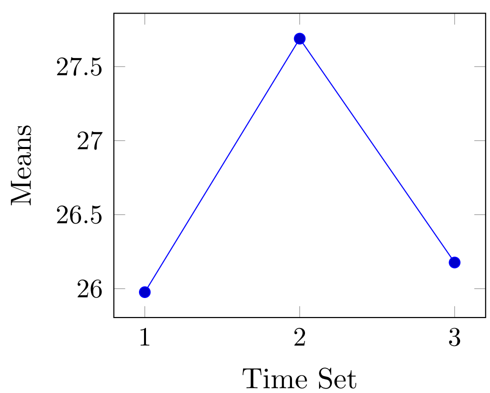
Elevation class 1



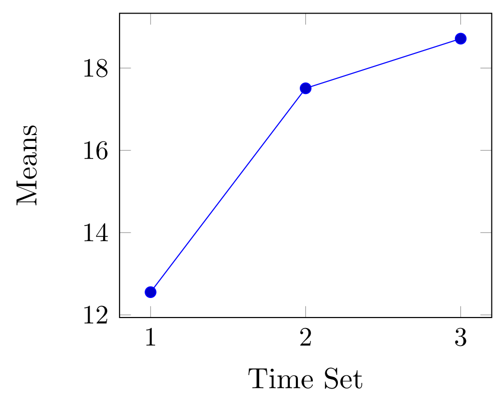

Elevation class 2



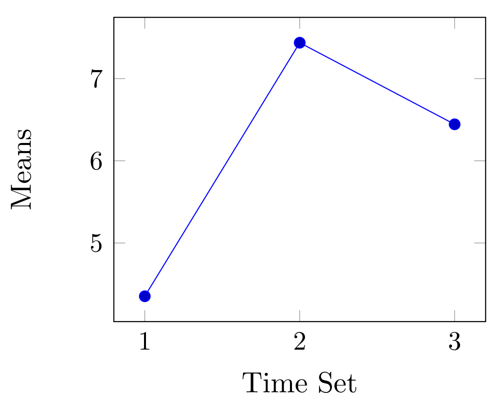

Elevation class 3



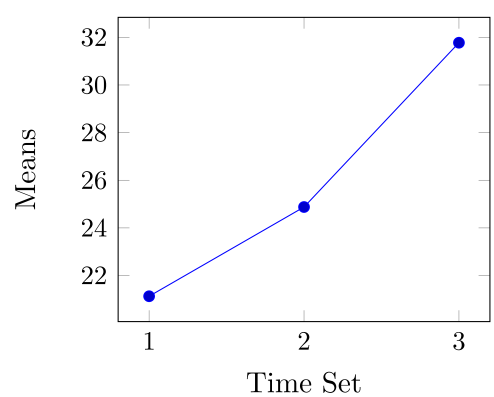

Elevation class 4



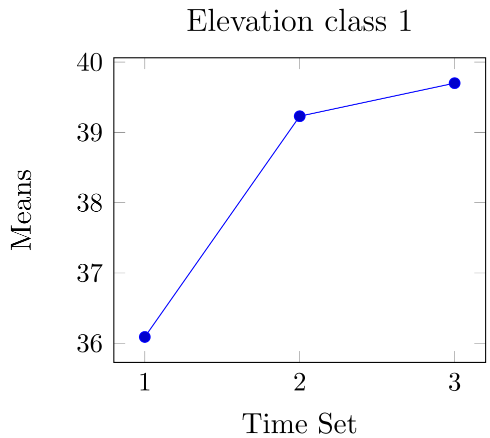

Elevation class 5

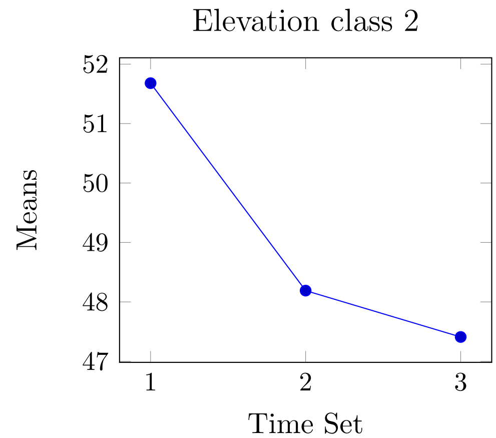


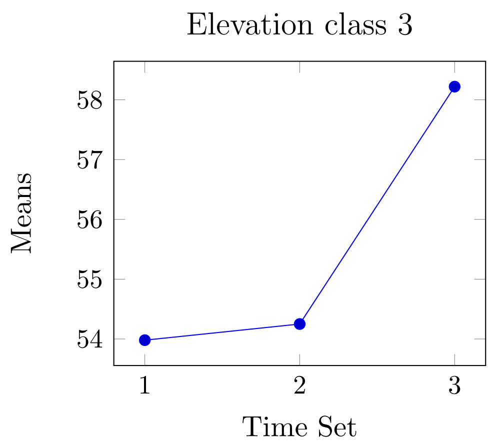

Elevation class 6

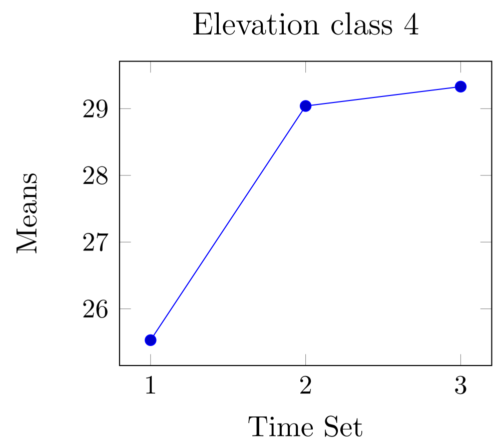


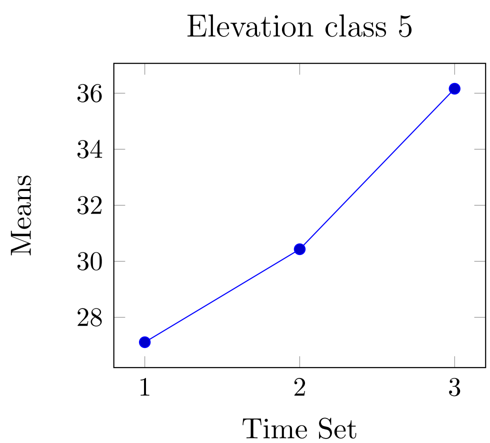
## E.4 Sulfate

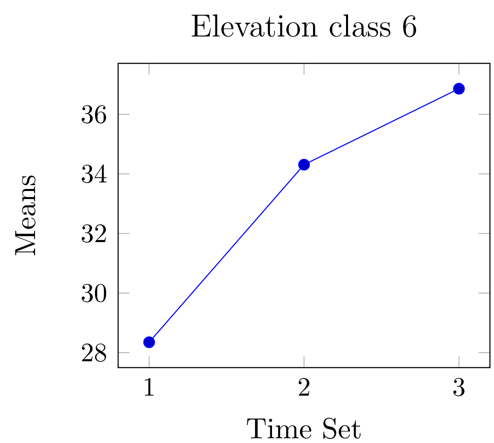

Elevation class 1
Means
40
39
38
37
36
1
2
3
Time Set


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($\theta$), cosine($\theta$), 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

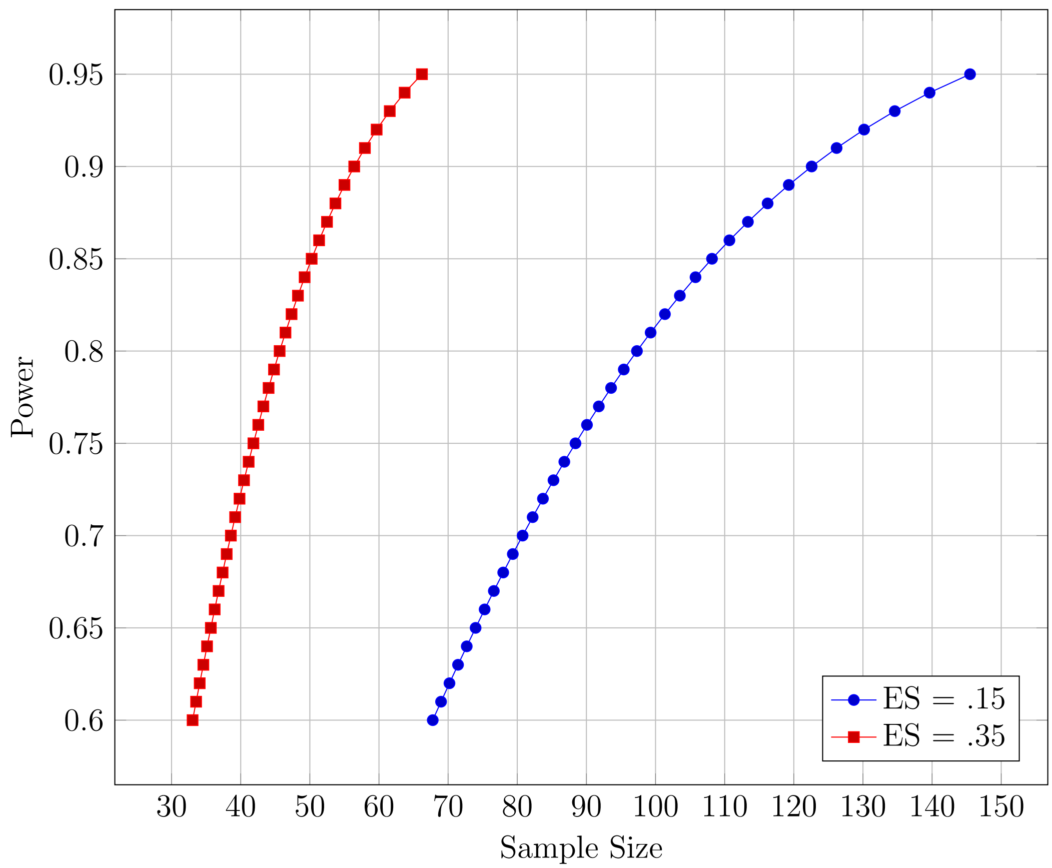



**Figure G.1:** pH Power Graph. The power is shown as a function of pH

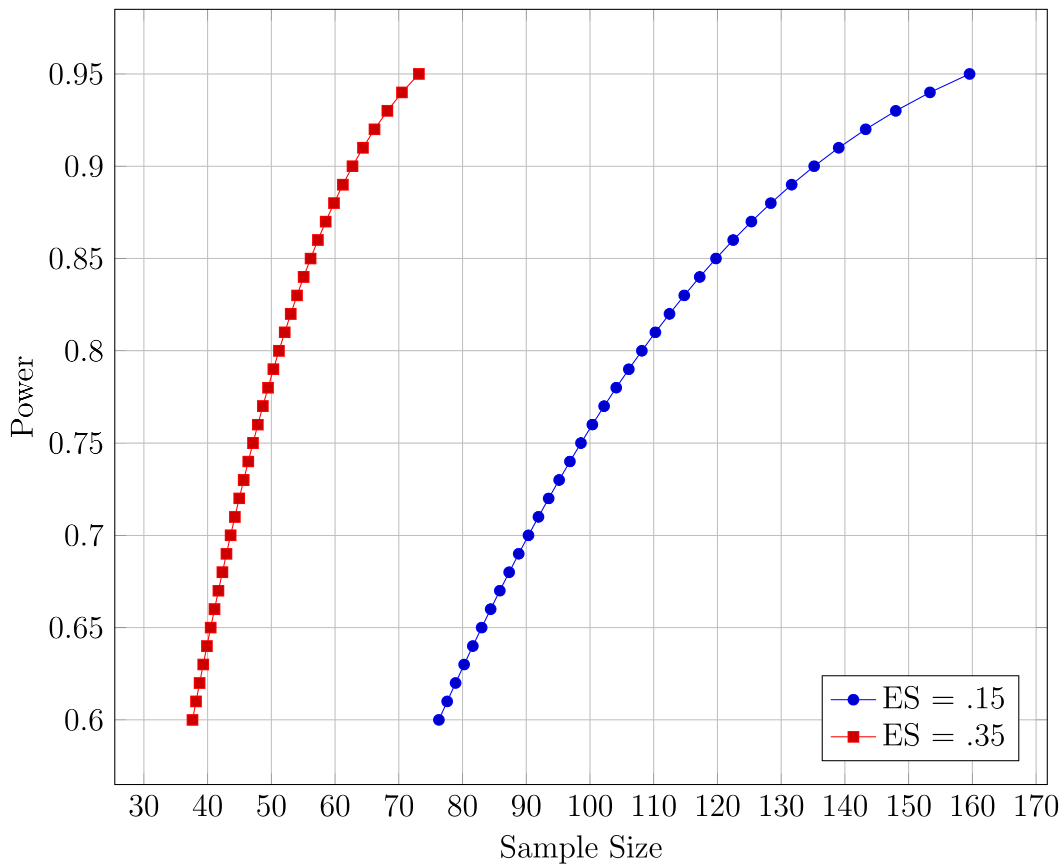



**Figure G.2:** ANC and Nitrate Power Graphs. The power graphs for ANC and Nitrate are the same because they both have the same number of predictors.

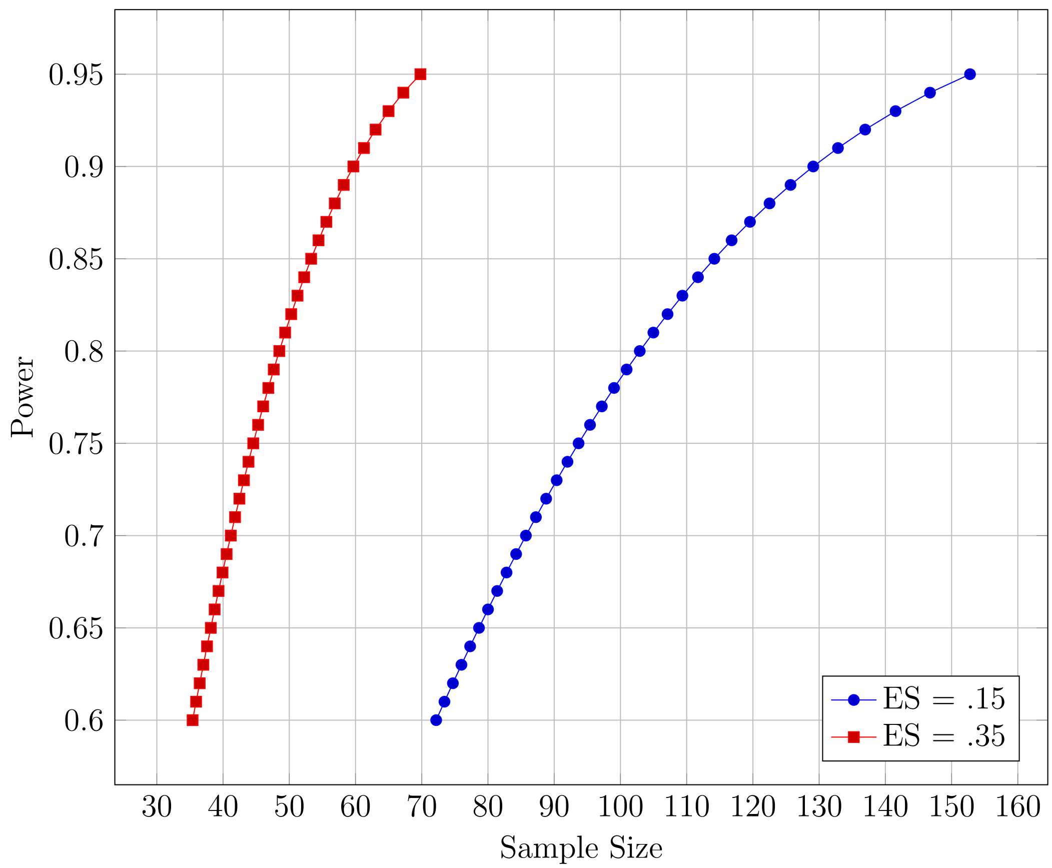



**Figure G.3:** Sulfate Power Graph

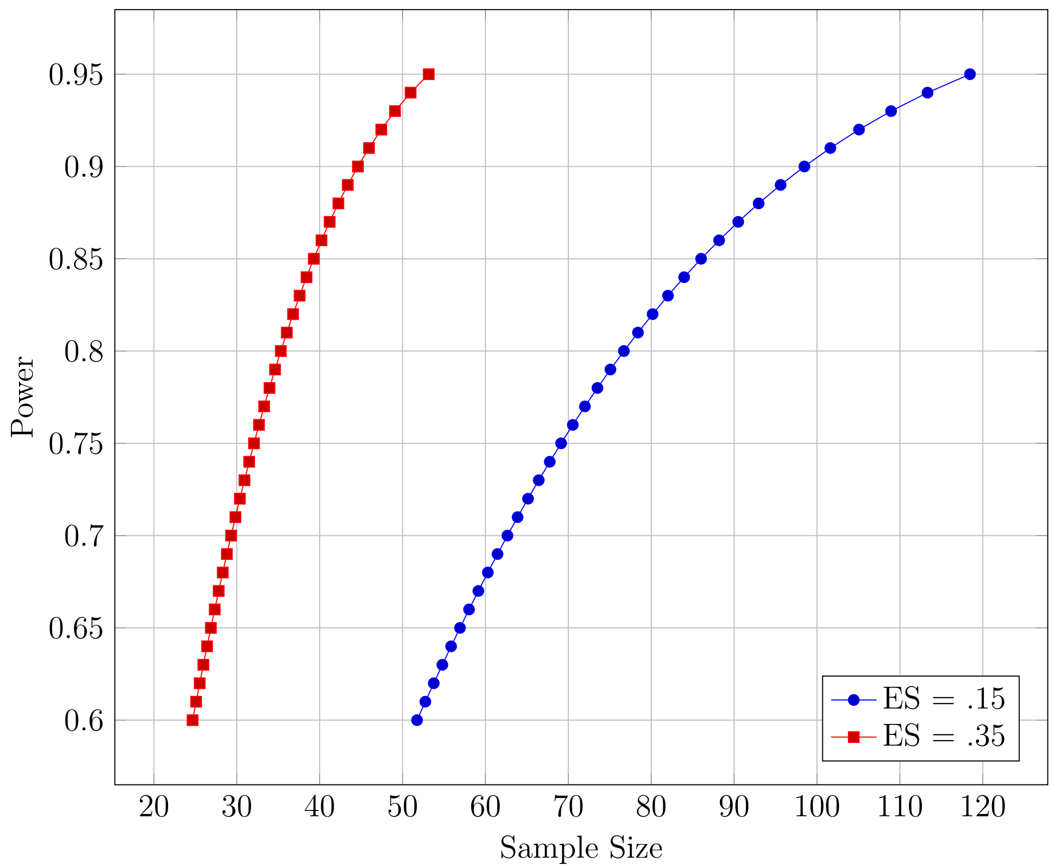



**Figure G.4:** Time Variables Power Graph

# 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.