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

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

To the Graduate Council:

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

Statistical Temporal Analyses on Legacy Data for the GRSM Stream Survey

A Thesis Presented for

The Master of Science

Degree

The University of Tennessee, Knoxville

Tim Pobst

May 2014

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Abstract

Abstract text goes here...

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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 and

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 research

Chapter 2

Trend Analysis

2.1 Methods

2.1.1 Introduction

- Trend analysis for Stream Survey has been done before and reported in (Robinson et al., 2008) and the Biotics effects report (Meijun Cai, 2012)
- A trend analysis of the data collected through the Stream Survey can be used to help determine the water quality of the streams
- The most important trend is the trend for pH
- Outline The trend analysis will be conducted on Stream Survey data spanning the years 1993-2012 using the statistical program JMP for determining outliers and the statistical program SPSS for the actual trend analysis.

2.1.2 Body

• A trend analysis will answer the continuing question concerning the overall health of the park which is, "How are the streams doing?". More specifically "Is the pH trending towards a higher pH or a lower pH?"

Data

- The data comes from years of analyzing water samples collected through the Stream Survey and is tabulated into a running data set.
- A single trend line could be made to encompass all 20 years worth of water quality data, but this would make discovering the cause of the trends more difficult.
- Assuming ecosystems try to achieve equilibrium the change observed over all time should be zero.
- So in order to easier learn from this trend analysis, it will be logically broken up into smaller sets of years.
- Different sets may have different positive or negative trends for which separate hypothesis have been or can be formulated and tested in this trend analysis.
- The separate data sets are between time and between elevation classes. There were three different time sets created. The first time set covers the years 1993 to 2002, these are the same years analyzed in (Robinson et al., 2008). The remaining years were broken up at 2008, which was the year that the Kingston and Bull run power plants installed scrubbers onto their stacks. So with the six different elevation classes and the three different time sets there are eighteen different data sets that are analyzed in this paper.

Instruments

- done usisng statistical programs.
- Outliler determination and trend hypothesis.

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

- Plot pH on y-axis vs. all time. This visually represents that the slope does not equal zero. Check outliers in this plot. If they can be explained then fix or delete them.
- Plot pH on y-axis vs. elevation. Visually check for trend of decreasing pH as elevation increases.
- Plot pH vs. month. To check for seasonality.
- Outliers found include Abrams, Anakeesta sites, and storm flow. Abrams is consistently found as an out lier within GRSM water quality projects using stream survey data for statistical purposes. Abrams is located in the Cades Cove area of the park and sits in natural limestone bedrock. This limestone increases the ANC of the streams so much that many of the measured Abrams pH values are high enough to be outliers and are thrown out of the data.
- Water quality at sites 237 and 252 are heavily influenced by Anakeesta geology introduced into the streams through road cuts.
- Storm flow is also usually seen as an out lier in past GRSM water quality projects. Storms can bring high intensity rain fall which can very quickly raise the levels of nitrate and sulfate pollution in the streams. The runoff

can also carry any pollutants that have come to rest on vegetation or the ground. The lowered pH of the streams caused by the storm flow can cause leeching of the surrounding mineral geology in affected areas. Healthy streams can rebound to normal pH values, unhealthy streams can have lowered ANC due to the leaching. Measurements taken from storm flow can show uncharacteristically low pH values and high amounts of metals. In this way storm flow is sometimes considered an out lier. Much of the water quality data has been characterized as base flow and storm flow by Dr.Cai, but not all it. Water quality data after 2010 has not been characterized. Dismissing all of storm flow as an out lier is complicated by this lack of information. Either; storm flow and base flow would need to be determined for the 2011 and 2012 data, all of the 2011 and 2012 data could be left out, or 2011 and 2012 would need to be characterized as base flow or storm flow. Throwing out the years 2011 and 2012 would leave the last time set with only two years of data. The data was compared with and without storm flow observations. It was determined to manually select out lier storm flow observations. They can be removed on a case by case basis during the regression procedure.

- review output for normality, heteroscedasticity, cook's D, DFBETAS,
 DFFITS.
- Find proposed out lier in original data
- Justify its removal, remove it and run the regression method again
- The outputs will change every time an observation is removed.
- The variable selected through this process were used to create fixed models to be used while discovering the Julian Date coefficient for each water quality variable in each data set.

Table 2.2: Equations created through step-wise variable selection

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

- If the step-wise equation had at least one time variable in it(Julian date, $\sin(\theta), \cos(\theta)$) then the rest were added. This is presented in Table C.1.
- along with the step-wise regression method, another regression analysis was done using only time based variables. These are the Julian Date, $\sin(\theta)$, and $\cos(\theta)$ time variables. This method was used to find trends in the water quality variables that are related to time only.
- IBM's SPSS was used to conduct this trend analysis.
- These options were chosen for regression and assumptions for this procedure include.(from notebook and textbook)

2.2 Results

• In (Robinson et al., 2008) table 4 reports julian date coefficients for four water quality variables (pH, ANC, NO₃, SO₄) by each elevation band.

- A similar layout was used in Table D.1 and Table D.2.
- This was done for continuity and ease of comparison.
- The first trend analysis was completed using the step-wise method for choosing predictors and the results are presented in Table D.1
- The second trend analysis uses only time based variables as predictors and these results are presented in Table D.2
- Both tables are modeled after table 4 in (Robinson et al., 2008)
- Each table is further divided into three different time sets: 1993-2002, 2003-2008, 2009-2012.
- Each of these time sets are further divided into six elevation bands
- Each of elevation band has the results of four trend lines, one for each of the studied water quality variables (pH, ANC, NO₃, SO₄).
- Each trend line is represented by its Julian date coefficient, the r² value for the trend line, and it's statistical significance.
- 2 of the 72 trend lines in Table D.1 are insignificant. In contrast only 20 of the trend lines in Table D.2 are significant.
- Insignificance is determined by receiving a p-value greater than .05, the α of the trend line. A p-value greater than .05 rejects the hypothesis that $\beta \neq 0$. There is greater than a 5% chance that β =0. There is to much chance of no trend line for the scientific community.
- Repeat trends from previous thesis
- Compare to (Robinson et al., 2008), his trends are negative.

2.3 Discussion

- Why were the trends insignificant?
- Why are the water quality trends trending the way they are at separate time sets (discuss comparisons between sets in the ANOVA bonferoni section).
- How should the water quality variables have behaved based on known properties and (Robinson et al., 2008).
- Very generally speaking these results are different than (Robinson et al., 2008) predicted.
- Water quality will continue to get better.
 - because pollution is being regulated
- there are still unknowns and prediction is still hard.

Chapter 3

Means Comparison

3.1 Methods

3.1.1 Introduction

Bull run and Kingston power plants installed scrubbers on their smokestacks in the year 2008 in order to decrease sulfate and nitrate emissions. These scrubbers have significantly reduced the amount of sulfur dioxide emitted by the smoke stacks. According to Figure 3.1, which is a bar chart depicting the sum of sulfur dioxide emissions of Kingston and Bull run power plants, the sulfur dioxide concentration dropped from 80 thousand tons in 2008 to about 15 thousand tons in 2009. Interestingly the through fall SO_4 concentrations dramatically decline from about $115 \mu eq L^{-1}$ in 2007 to about $30 \mu eq L^{-1}$ in 2010. The hypothesis is that the decrease in sulfur dioxide emissions could correlate to the decrease in SO_4 concentrations measured in Noland Divide through fall. And assuming that the sulfur dioxide emissions from Kingston and Bull run power plants affect the whole GRSM park then there may be signals for this affect in the data. To examine this each time set will be tested against each other by way of means comparison methods.

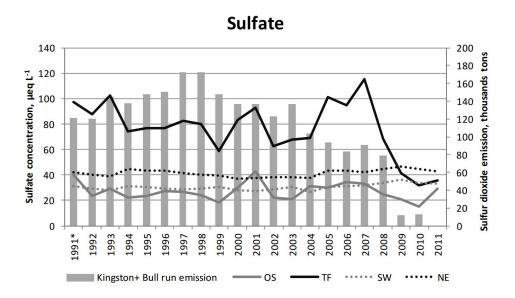


Figure 3.1: Sulfate emmisions of Kingstion and Bull run against those measured in Noland high elevation site (UTK, 2012).

Instruments

ANOVA is the standard means comparison method. But it cannot compare more than two groups at once, and a method is needed that can compare all three time sets. The Bonferroni multiple comparisons method is an option in the SPSS statistical program and can compare more than two groups at a time. The explanation of the Bonferroni method given by the SPSS manual is that this method uses t tests to perform pairwise comparisons between group means and that the observed significance level is adjusted for the fact that multiple comparisons are being made (IBM, 2013).

The Bonferroni method will create two specific types of outputs. The first is a line graph showing the means of each group analyzed. And the second is a table of pairwise listings of all the groups compared to each other. This table contains 95% confidence intervals and the significance associated with each comparison. These confidence intervals are produced by the difference in means between the two groups being compared. If the confidence interval includes zero then the groups are statistically the same or equal.

Using SPSS and the Bonferroni method three time sets (93-02, 03-08, 09-12) will be compared at six elevation class levels and across four water quality variables (pH, ANC, NO₃, and SO₄). Each group compared is the same stream survey data analyzed in chapter 2 and chapter 4 of this paper.

3.2 Results

Table 3.1: Bonferoni comparisons between multiple groups

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

Table 3.1 reports the Bonferoni comparison means between the four water quality variables (pH, ANC, NO₃, SO₄) in one time set against the same water quality variable in another time set by elevation bands. In the table there are three columns per water quality variable. And each column represents the comparison of two groups of the same variable in different times. If the Bonferroni comparison found the groups to be equal then equality was represented by an equal sign. If the groups are not equal an not equal sign was used to show this. All groups that were found to be equal were

insignificant and all groups that were unequal are significant at the 0.05 α level. The bonferoni figures are presented in section E.1. There are six figures for each of the water quality variables, one for each of the elevation classes. For the most part the figures representing pH seem to be continuing a similar rate of change through the years, but this is also misleading because the time sets do not contain equal numbers of years.

The set comparisons between pH are the first comparisons presented. pH contains more unequal sets than any other water quality variable. Mostly all the sets are different except between elevation class 2 which is all the same and class 4 and 6 which show sets 1 and 2 being equal. If a pronounced elevational trend existed for pH in the GRSM, this trend would be visible in the Bonferroni figures. Following the means of each time set through the different elevation classes the largest mean should be in elevation class 1 and the smallest in elevation class 6. Unfortunately elevation class 2 alway contains the lowest means instead of Elevation class 6. And elevation class 3 behaves as if it should be between elevation class 5 and 6.

In contrast to the pH figures, the ANC figures do not all have similar rates of change. In the odd numbered classes ANC reached a peak in set 2 and dropped for set 3. All of the ANC figures have a decreasing trend from set 2 to 3 except for class 2 which is steadily increasing. The comparison found a lot of equality between the means of the ANC sets. Elevations 1, 4, and 6 are all equal. At elevations 2 and 3 set 1 and 3 are the only sets that are unequal. And at elevation 5 sets 1 and 2 are equal but set 3 is not. The set means presented in the ANC figures vary greatly in concentration. Classes and 1 and 2 are more than double the means of the other classes. The ANC concentrations of elevation class 2 are the lowest which helps explain why the pH of elevation class 2 is also the lowest. It is important to note here that even though class 2's concentrations are the lowest, they are also the only concentrations that are increasing.

For NO_3 elevation classes 4 and 6 are all the same and elevation 3 shows sets 1 and 2 being equal where 3 is not. Elevation class 1 is the opposite of expected showing all

being equal except for sets 1 and 2. In elevation class 2 sets 3 and 2 are equal and in elevation class 5 sets 3 and 1 are equal. The odd numbered figures for NO₃ all have decreasing mean values from set 2 to 3. In elevation classes 2 and 4 the mean values for set 3 are higher than those in set 2 but the rate of increase is slowing. Elevation 6 is always increasing. The NO₃ figures show mostly decreasing concentrations over time, except for class 6. The odd classes all have decreasing negative trends from set 2 to set 3 while classes 2 and 4 have decreasing positive trends between set 2 and 3.

SO₄ shows all three sets being equal across all elevation classes except for class 2. Class 2 shows only sets three and two being equal. These figures can sometimes be misleading when visually comparing groups and it is always best to have the confidence intervals on hand. For example when looking at the SO₄ figures many of the means look different across the time sets, but according to the table, except for class 2, they are all equal across time sets. All of the set 3 means for SO₄ are larger than their respective set 2 means except for those in class 2 which has negative trends throughout.

3.3 Discussion

Because this analysis was completed after the trend analysis and descriptive statistics for these data sets were available certain results were expected. Such as the increase in pH over time and the abnormal ANC concentrations. The apparent decrease in ANC overtime as indicated in the Bonferroni figures was unexpected both because this is in contrast to the Julian date coefficients for ANC and pH has an increasing trend overtime. Because the Bonferroni method calculates significant means for the water quality vector the difference between the figures and the trends suggests error in the trend analysis models.

The focus of this chapter was to investigate the decline in sulfur dioxide emissions from the Kingston and Bull run power plants and how it may impact the decline in SO_4 concentrations in the through fall measurements of the Noland divide high elevation

site. If a correlation existed it would be apparent in the pH results, but especially in the SO₄ results. A significant negative difference in means for set 3 compared to sets 1 and 2 would support the hypothesis. The inequalities present between the sets of pH data display a possible connection to the decline in sulfur dioxide pollution but there are many other factors that effect stream pH. The comparisons between the SO₄ sets are unfortunately mostly equal. This suggests a bank of SO₄ with a more steady output evidenced in the measured stream concentrations versus the quickly declining emissions measured as proposed input. The pollution is taken in by the forest and slowly released into the streams. More time may be needed to see affects of the scrubbers.

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 r², number of predictors, and Effect size. N and adj.r² 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 r² 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, 1992a).
- 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 the 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, 1992a)
 "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, NO₃,SO₄). Taken from the earlier step-wise selection method (link to step-wise table). Therefore only one "power graph" is needed for every trend line in each variable.
- ES and power can be chosen or kept constant based on reports by Cohen.
- Cohen's standardizations
- While the "power graphs" are useful in planning for the future of the stream survey, it can be shown that if ES and power are chosen, exact numbers of samples and sites can be added and subtracted from elevation bands.

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

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

• The rest was done in excel

- This calculated number of observations can be divided by the number of samples
 collected in one year to get the number of years required to reach a power of
 .80.
- The analysis can be further conducted by calculating the number of samples per year to achieve a power of .80. For this calculation all water quality variables were given the highest number of samples of 110 and 77 was used for the trends using only time variables.

Table 4.2: samples/year to achieve a power .80 (N_b)

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

- ?? is needed to calculate number of samples needed per elevation band to achieve a power of .80. This number of samples can then be further divided to get a number of sites needed to achieve a power of .80. If a trend line with a power of .80 is desired after one year ,for all water quality variables to be satisfied, 110 samples need to be collected. If four years are waited then only 28 samples need to be collected per year.
- To create this final table the number of samples per elevation band was subtracted from the number of samples to achieve a power of .80 which gives us the number of samples needed in addition to what is currently collected to receive a power of .80. These results are organized into samples needed per elevation band to achieve a power of .80 and seperated by years depending of how many years of data go into the trend lines.

4.2 Results

4.2.1 Post hoc

- A post hoc power analysis was conducted for each of the two methods of trend analysis.
- Table F.1 and Table F.2 record the results of the post hoc analysis on the trend lines with variables created through the step-wise method and the trend lines created using only time variables respectively. Included in these tables are the number of samples and r² 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, NO₃,SO₄) 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, 1992a). 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	рН	ANC NO ₃	SO_4	Time variables
1	13,23,24,30,479	26	3.77	4.19	3.96	2.96
2	4, 311, 268, 480, 310,	34	2.88	3.21	3.03	2.26
	483, 147, 148, 484					
3	114, 481, 482, 149,	62	1.58	1.76	1.66	1.24
	66, 492, 137, 293, 270,					
	493, 485, 144, 224					
4	143, 142, 73, 71	24	4.08	4.54	4.29	3.21
5	74, 221, 251, 233	22	4.45	4.95	4.68	3.50
6	253, 234	12	8.17	9.08	8.58	6.42

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

- ?? records the six elevation bands along with the site numbers that belong to them. In the column labeled ,current n per year, the amount of samples collected per elevation band in the year 2012 was tabulated. The values in the remaining columns were calculated by dividing the number of samples given in ?? by the current samples per year column in ??.
- Looking at the table there are 26 samples collected in elevation band one in one year. In order to compute a trend line that receives a power of .80 with pH as the dependent samples would need to be collected for 3.77 years before the trend line is computed. The larges is elevation class for a trend line in ANC or NO₃ 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 r² 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 r² values. The low r² 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 reevaluated 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.
- Cohen, J. (1992a). A power primer. Psychological bulletin, 112(1):155. 18, 19, 23
- Cohen, J. (1992b). Statistical power analysis. Current directions in psychological science, 1(3):98–101.
- Helsel, D. R. and Hirsch, R. M. (1992). Statistical methods in water resources, volume 49. Elsevier.
- IBM (2013). Ibm spss statistics base 22. 12
- 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
- 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.

- 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*.
- 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, 5, 8, 9, 10, 27
- UTK (2012). 2011 water quality annual report. Technical report. x, 12
- 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.

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

 $\textbf{Table A.1:} \ \, \textbf{GRSM Stream Survey site descriptions}$

	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		I	bН			ANC	ANC meql			Nitra	Nitrate meql			Sulfa	Sulfate meql	
		N	Minimum	Maximum	Mean	N	Minimum	Maximum	Mean	N	Minimum	Maximum	Mean	N	Minimum	Maximum	Mean
1993- 2002																	
	П	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
	က	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
	ಬ	116	6.07	7.05	6.50	116	41.34	162.76	77.06	99	1.23	10.55	4.35	116	7.51	79.98	26.14
	9	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
	က	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
	ಬ	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
	9	26	5.79	7.05	6.44	26	6.73	130.63	55.68	86	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
	က	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	26	6.20	7.08	6.68	26	25.70	107.58	64.13	26	0.54	34.67	18.72	26	19.89	46.66	29.33
	ಬ	56	6.30	7.11	6.77	56	40.10	115.94	73.55	56	0.21	83.68	6.44	56	16.78	109.18	36.16
	9	92	4.24	7.09	6.52	92	-3.92	114.28	46.15	92	0.16	79.04	32.17	92	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.

		Depen	dents for	step-wise	e regression
Available Variables	comments	рН	ANC	NO_3	SO_4
рН	Dependent				
ANC	Dependent			X	X
NO_3	Dependent	X	X		X
SO_4	Dependent	X	X	X	
Julian Date			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 of (p-value)	coefficient, eq/L or	pH units (model a	djusted r^2)
		. ,		pН	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
_000 _000	-	(1000-2000)	9	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)	Ü	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)	10	0.663	0.996	0.637	0.923
		(2000 0000)		0.000	0.000	0.000	0.000
	4	914.4-1066.8	4	0.249	-0.028	0.092	0.110
	1	(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
-000 -01-	-	(1000-2000)	9	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)	Ü	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)	-5	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
	U	(4500<)	_	0.286	0.809	0.881	0.861
		()		0.000	0.000	0.000	0.000
				39			

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 c (p-value)	oefficient, eq/L or	pH units (model a	djusted r^2)
				pН	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	$\boldsymbol{0.142}$
	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
	2	1051 0	~	.100	0.047	0.006	0.331
	6	1371.6<	2	.156 .096	-0.016	$-0.208 \\ 0.092$	-0.036 -0.009
		(4500<)		.096	$0.075 \\ 0.863$	0.092 0.058	-0.009 0.707
2003-2008	1	304.8.600.6)	5	.139	0.009	0.155	0.192
2005-2008	1	304.8-609.6) (1000-2000	Э	0.040	0.009 0.001	$0.155 \\ 0.061$	0.192
		(1000-2000		0.040 0.025	0.888	0.012	0.043
	2	609.6-762	9	0.145	-0.090	0.178	0.138
	-	(2000-2500)	v	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	$0.046 \\ 0.020$	$0.074 \\ 0.002$
0000 2012	-	204.0.200.2		0.041	0.274		
2009-2012	1	304.8-609.6 (1000-2000)	5	$0.111 \\ 0.028$	$0.026 \\ 0.000$	$-0.036 \\ 0.018$	$-0.092 \\ 0.005$
		(1000-2000)		$0.028 \\ 0.122$	$0.000 \\ 0.718$	0.018 0.619	$0.005 \\ 0.207$
	2	609.6-762	9	0.141	0.017	0.020	-0.062
	4	(2000-2500)	Э	0.141 0.052	0.056	0.020 0.011	-0.010
		(2000 2000)		0.037	0.800	0.767	0.376
	3	762-914.4	13	-0.034	-0.027	-0.036	0.078
	,	(2500-3000)	10	-0.009	-0.002	-0.004	-0.007
		`/		0.611	0.684	$\boldsymbol{0.592}$	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



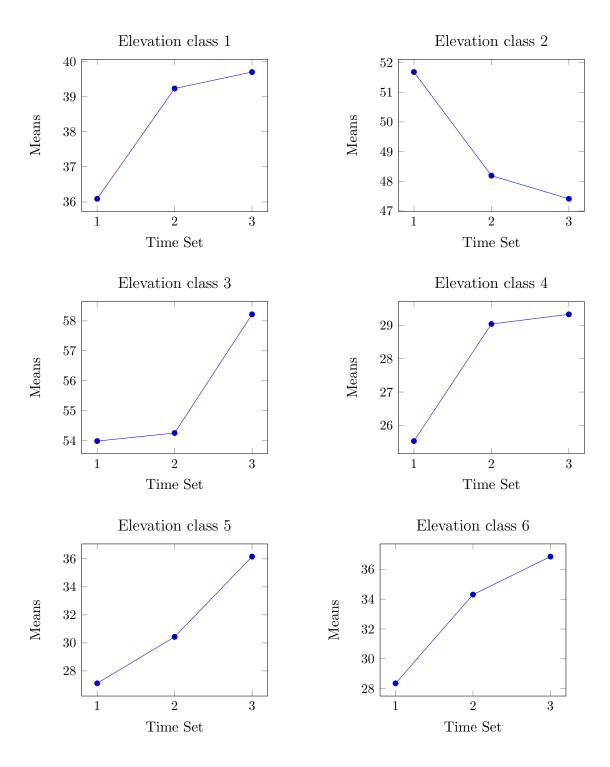
E.2 ANC



E.3 Nitrate



E.4 Sulfate



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.

				Hd			ANC	ANCmeqL			Nitra	NitratemeqL			Sulfat	SulfatemedL	
Set	Class	Z	$ \begin{array}{c} {\rm Adjusted} & {\rm Effect} \\ {\rm r}^2 & {\rm Size} \end{array} $	Effect Size	Actual Power	Z	$\underset{\mathbf{r}^2}{\mathrm{Adjusted}}$	Effect Size	Actual Power	Z	$\underset{\mathbf{r}^2}{\operatorname{Adjusted}}$	Effect Size	Actual Power	Z	$\underset{\mathbf{r}^2}{\operatorname{Adjusted}}$	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
	က	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	99	0.328	0.49	0.98	116	0.566	1.30	1.00
	9	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																	
	П	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
	က	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
	9	26	0.317	0.46	1.00	26	0.812	4.32	1.00	86	0.832	4.95	1.00	101	0.844	5.41	1.00
2009-																	
	П	191	0.894	8.43	1.00	191	0.989	89.91	1.00	191	0.376	09.0	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
	က	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	26	0.593	1.46	1.00	26	0.772	3.39	1.00	26	0.635	1.74	1.00	26	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
	9	92	0.286	0.40	0.99	92	0.809	4.24	1.00	92	0.881	7.40	1.00	92	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.

		Hd			ANC	ANCmeqL			Nitrat	NitratemeqL			Sulfat	SulfatemedL	
Z	$ \begin{array}{c} {\rm Adjusted} & {\rm Effect} \\ {\rm r}^2 & {\rm Size} \end{array} $	Effect Size	Actual Power	Z	$\underset{\mathbf{r}^2}{\operatorname{Adjusted}}$	Effect Size	Actual Power	Z	$\underset{\mathbf{r}^2}{\operatorname{Adjusted}}$	Effect Size	Actual Power	Z	$\underset{\mathbf{r}^2}{\text{Adjusted}}$	Effect Size	Actual Power
327	0.047	0.049	0.93	327	0.024	0.03	0.65	275	0.016	0.02	0.39	325	0.045	0.05	0.92
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
400	0.013	0.01	0.46	398	0.000	0.00	90.0	365	-0.004	NA	NA	391	-0.004	NA	NA
121	0.059	90.0	0.61	120	0.294	0.42	1.00	105	-0.027	NA	NA	119	-0.016	NA	NA
116	0.051	0.05	0.52	116	0.381	0.62	1.00	99	0.120	0.14	0.68	116	-0.010	NA	NA
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
255	0.040	0.04	0.78	255	0.001	0.00	0.02	252	0.061	90.0	0.94	261	0.043	0.04	0.82
289	0.061	90.0	0.96	289	0.081	0.09	0.99	296	0.043	0.04	0.87	298	0.014	0.01	0.37
299	0.020	0.02	0.52	299	-0.003	NA	NA	297	-0.003	NA	NA	308	0.006	0.01	0.18
119	0.148	0.17	0.97	119	0.180	0.22	0.99	121	0.086	0.00	0.80	123	0.023	0.02	0.26
35	-0.069	NA	NA	35	0.337	0.51	0.93	30	-0.082	NA	NA	37	-0.024	NA	NA
26	0.081	0.00	0.67	26	0.094	0.10	0.74	86	0.046	0.05	0.40	101	0.074	0.08	0.64
191	0.028	0.03	0.47	191	0.000	0.00	0.02	191	0.018	0.02	0.31	190	0.005	0.01	0.11
212	0.052	0.05	0.82	212	0.056	90.0	0.85	212	0.011	0.01	0.22	212	-0.010	NA	NA
228	-0.009	NA	NA	228	-0.002	NA	NA	228	-0.004	NA	NA	228	-0.007	NA	NA
26	0.200	0.25	0.99	26	0.161	0.19	0.96	26	-0.016	NA	NA	26	-0.011	NA	NA
56	0.218	0.28	0.58	29	0.466	0.87	0.98	29	-0.039	NA	NA	29	-0.076	NA	NA
92	0.039	0.04	0.27	92	0.058	90.0	0.39	92	-0.016	NA	NA	92	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 $\,$

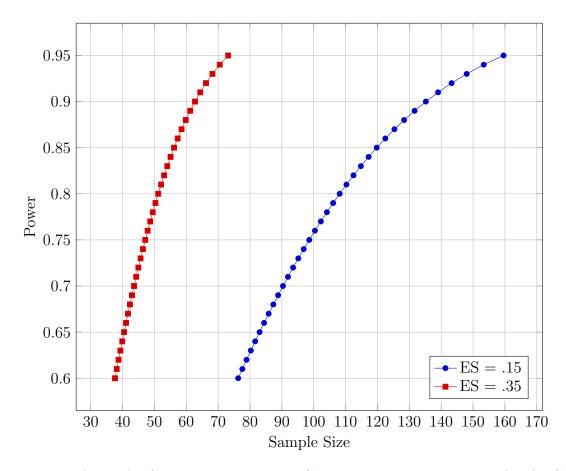


Figure G.2: ANC and Nitrate Power Graphs. The power graphs for ANC and Nitrate are the same because they both have the same number of predictors.

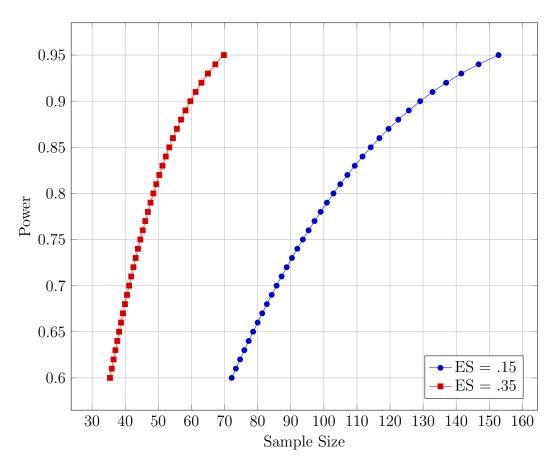


Figure G.3: Sulfate Power Graph



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.