

Statistical Analyses on Legacy data of the GRSM Stream Survey

Time Trend Analysis, ANOVA, Power Analysis

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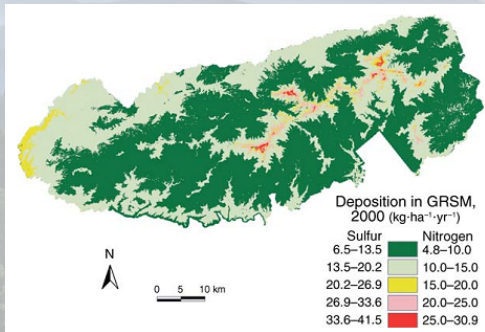
Description of study area

- Straddles the border of Tennessee and North Carolina
- Diverse wildlife, plant life, and fisheries.



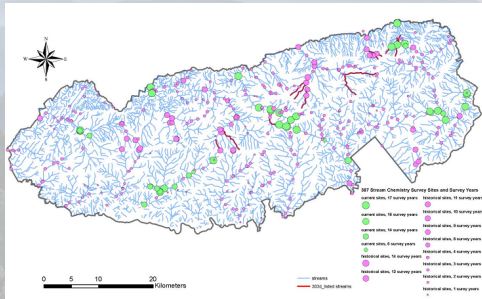
Acid Deposition and the GRSM

- Acid deposition negatively affects the park.
- Higher elevations are effected worse.



Database

- 1993 - ?
- The number of sites monitored has decreased over the years



Elevation Bands

- 11 historical elevation bands
- re-organized into six more powerful bands

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

Time sets

- 1 1993-2002: The years previously studied by Dr. Robinson
- 2 2003-2008: Up to 2008, the year Kingston and Bull-run installed sulfate scrubbers
- 3 2009-2012: After the scrubbers were installed up to the most recent data available

pH and Acid Anion Time Trends in Different Elevation Ranges in the Great Smoky Mountains National Park

R. Bruce Robinson¹, Thomas W. Danner², Glenn R. Harwell³, Stephen C. Moore⁴, Matt Kulp⁵, and John S. Schwartz⁶

ABSTRACT: Quarterly base flow water quality data collected from October, 1993 to November, 2002 at 98 stream sites in the Great Smoky Mountains National Park were used to integrate multiple linear regression models to analyze pH, acid neutralizing capacity (ANC), and sulfate and nitrate long-term time trends. The potential predictor variables included elevation, basin size, seasonality, elevation, basin slope, stream order, precipitation, average streamflow, geology, and acid deposition fluxes. Modeling revealed statistically significant decreasing trends in pH and sulfate with time at lower elevations, but generally no long-term time trends in stream nitrate or ANC. The best forecasting models were chosen based on maximizing the r^2 of a full-term data set. If conditions remain the same and past trends continue, the forecasting models suggest that 50% of the sampling sites will reach pH values less than 6.0 in less than 30 years, 63.3% in less than 27 years, and 96.7% in less than 30 years. The pH forecasting models explain 67% of the variability in the full-term data.

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CE Database subject headings: Acid rain; pH; Regression analysis; Time series analysis; Water quality; Monitoring; Watersheds; Mountains.

Introduction

The Great Smoky Mountains National Park (GSMNP) has more than 3,600 km² (1,390 mi²) of stream, including five streams designated as Outstanding National Resource Waters. GSMNP stream segments are good examples of aquatic systems, and its headwaters are considered some of the best in the eastern United States. The GSMNP also contains some of the highest amounts of acid deposition amongst all national parks, and the pH of precipitation (Shehadeh et al. 1993) is about 4.5 in the GSMNP region (GSMNP 1996). The acidic deposition causes serious concern for stream impairment because the GSMNP's geology lacks significant buffering capacity [50% of all measured stream sites have acid neutralizing capacity (ANC) less than 300 µeq/L, and 70% have less than 10 µeq/L, and 17% have a base flow pH less than 6.0]. In comparison, Danner et al. (2003) stated that aquatic biota living in surface waters having a pH of less than 6, ANC less than 10 µeq/L, or aluminum concentrations greater than 3 µeq/L, are at risk from surface water acidification. Sulfate and nitrate are closely associated with acid deposition, but at least one major elevation watershed in the GSMNP is believed to be in Stage 2 nitrogen saturation (Shehadeh 1995), with elevated stream nitrate values in three stream years round (Shehadeh et al. 1995, van Margent et al. 2003). Importantly, some GSMNP streams that once supported native brook trout populations as recently as 30 years ago no longer do, and acid deposition is suspected to have some related to their extirpation.

Because of the potential impact of acid deposition, long-term base flow stream water quality monitoring began in 1993. Data are available from a network of 98 stream sites with enough historical record to assess long-term water quality trends (Fig. 1). The objectives of this study were to:

1. Determine if pH, ANC, sulfate, and nitrate are increasing or decreasing with time in select GSMNP streams, i.e., to determine how much of the variability in water quality is not explained by long-term trends themselves related to its own trends.
2. Determine if there are differences in time trends for pH, ANC, sulfate, and nitrate within different elevation zones.
3. Determine if statistically significant forecasting models for stream pH, ANC, sulfate, and nitrate can be developed.

Background

The 1990 and 1990 Amendments of the Clean Air Act (CAA) have resulted in declines of gross pollutant emissions and CAA

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Time sets

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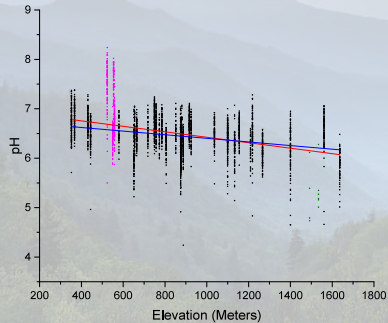
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Data Smoothing

- Outliers and Influential observations
- Removed Abrams and sites associated with Anakesta



Objectives

One

Determine conditions of stream pH and acidic anions within elevation bands.

- Time trends
- Means Comparisons

Two

Determine statistical power for water quality parameters.

- Post Hoc Analysis
- A priori Analysis

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Stream Survey trend analysis history

Robinson 2008

- Time trends for water quality variables were computed for 90 sites in 10 elevation bands for the years 1993 to 2002.
- Predictions for stream pH

Results

pH is **decreasing** at at rate of -0.0127 to -0.0260 pH units/year for Elevation Classes 2-6.

Biotics Effects report 2013

- Time trends for water quality variables were computed for 67 sites for the years 1993 to 2009.

Stream Survey trend analysis history

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Results

pH will reach a deadly **5.0** in 9.4 years in elevation class 6 (914-1067m)

Biotics Effects report 2013

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Stream Survey trend analysis history

Robinson 2008

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Results

- Most showed no trend
- 22 showed an **increase** in pH
- Only 2 showed a **decrease**

Biotics Effects report 2013

- Time trends for water quality variables were computed for 67 sites for the years 1993 to 2009.



Two equation methods

Step-wise: $Y = \beta_0 + \beta_1 T + \beta_2 X + \beta_n X + \epsilon$

- Multi-step process of adding and removing variables
- A variable with an F test statistic of .05 or higher can enter but would be removed if it exceeded .10.
- If any of the time variables were chosen by the step-wise method, the others were forced in.

Time Variables: $Y = \beta_0 + \beta_1 \text{JulianDate} + \beta_2 \sin(\theta) + \beta_3 \cos(\theta) + \epsilon$

- Remove the confusion caused by extra non-time based variables
- Inherently weaker because time doesn't explain all the variation of the dependent variables.

Step-wise equations

Dependent (n)	Model	Adjusted r^2	Model p
pH (3116)	.673 $\times \log_2(\text{Sum Base Cations}) + (-.368 \times \text{NO}_3) + (.262 \times \text{Julian Day}) + (-.266 \times \text{SO}_4) + (-.050 \times \cos(\theta))$	0.630	<0.001
ANC (3116)	(.415 $\times \text{Sum Base Cations}) + (-.185 \times \text{SO}_4) + (.595 \times \text{Conductivity}) + (-.102 \times \text{NO}_3) + (.019 \times \text{Julian Date}) + (.005 \times \text{Cl}) + (.005 \times \sin(\theta))$	0.984	0.049
NO ₃ (3116)	(-.295 $\times \text{SO}_4$) + (-3.183 $\times \text{ANC}$) + (2.19 $\times \text{Conductivity}$) + (.923 $\times \text{Sum Base Cations}$) + (.120 $\times \text{Julian Date}$) + (.051 $\times \text{Cl}$) + (.047 $\times \sin(\theta)$) + (.031 $\times \cos(\theta)$)	0.498	0.017
SO ₄ (3116)	(-.166 $\times \text{NO}_3$) + (2.318 $\times \text{Conductivity}$) + (-3.229 $\times \text{ANC}$) + (1.033 $\times \text{Sum Base Cations}$) + (.042 $\times \text{Julian Date}$)	0.720	<0.001

Step-wise equations

- pH **increasing**
- ANC **increasing**
- Nitrate **increasing**
- Sulfate **decreasing**

Trend Results

- pH is **negative** in only 3 significant lines, all in the 93'-02' time set, in elevation classes 2, 3, and 5
- Overall pH is **increasing** over time

Time Variables

Only 20 of the 72 trends are significant

- pH **increasing**
- ANC **increasing**
- Nitrate
- Sulfate

Step-wise equations

- pH **increasing**
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Time Variables

Only 20 of the 72 trends are significant

- pH **increasing**
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- Nitrate
- Sulfate

Trend Results

- Eleven **positive** trends ranging from 0.005 to 0.901 μeqL^{-1}
- Seven **negative** trends ranging from -0.002 to -0.082 μeqL^{-1}
- Overall ANC is **increasing** over time

Step-wise equations

- pH **increasing**
- ANC **increasing**
- Nitrate **increasing**
- Sulfate **decreasing**

Time Variables

Only 20 of the 72 trends are significant

- pH **increasing**
- ANC **increasing**
- Nitrate
- Sulfate

Trend Results

- Trends for time set 1 are half **positive** and half **negative**
- Trends in set 2 are all **positive**, from 0.038 to 0.204 μeqL^{-1}
- There is only one **decreasing** trend in set3, class 4 (-0.013 μeqL^{-1})
- Overall nitrate is **increasing** over time

Step-wise equations

- pH **increasing**
- ANC **increasing**
- Nitrate **increasing**
- Sulfate **decreasing**

Time Variables

Only 20 of the 72 trends are significant

- pH **increasing**
- ANC **increasing**
- Nitrate
- Sulfate

Trend Results

- All trends are **positive** in set 2, ranging from 0.034 to 0.161 μeqL^{-1}
- Trends in set 3, classes 1, 3, and 6 are **negative**
- Trends are **increasing** from set 1 to set 2, but **decreasing** from set 2 to set 3

Step-wise equations

- pH **increasing**
- ANC **increasing**
- Nitrate **increasing**
- Sulfate **decreasing**

Time Variables

Only 20 of the 72 trends are significant

- pH **increasing**
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Trend Results

- Set 1 contains 0 significant lines and together sets 2 and 3 are half insignificant
- Other than prevalent insignificance, the trends for the time variables are similar to those of the the step-wise equations
- Overall pH is slowly **increasing** over time

Step-wise equations

- pH **increasing**
- ANC **increasing**
- Nitrate **increasing**
- Sulfate **decreasing**

Time Variables

Only 20 of the 72 trends are significant

- pH **increasing**
- ANC **increasing**
- Nitrate
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Trend Results

- Only 2 of the 24 trends are significant
- Set 1, class 5 has a **decreasing** trend of $-0.148 \mu\text{eqL}^{-1}$
- Set 3, class 5 has a **increasing** trend of $0.891 \mu\text{eqL}^{-1}$
- Overall ANC is **increasing** over time

Step-wise equations

- pH **increasing**
- ANC **increasing**
- Nitrate **increasing**
- Sulfate **decreasing**

Time Variables

Only 20 of the 72 trends are significant

- pH **increasing**
- ANC **increasing**
- Nitrate
- Sulfate

Trend Results

- Only 6 of the 24 trends are significant, 2 in set 1, 4 in set 2, 0 in set 3
- Every trend is **increasing** except set 1, class 1, which is $-0.138 \mu eq L^{-1}$
- The increasing trends range from $0.155 \mu eq/L$ to $0.330 \mu eq L^{-1}$
- Overall nitrate is **increasing** over time
- The trends are **decreasing** from set 2 to 3, but all of set 3 is insignificant

Step-wise equations

- pH **increasing**
- ANC **increasing**
- Nitrate **increasing**
- Sulfate **decreasing**

Time Variables

Only 20 of the 72 trends are significant

- pH **increasing**
- ANC **increasing**
- Nitrate
- Sulfate

Trend Results

- Only 5 of the 24 trends are significant, 1 in set 1, 4 in set 2, 0 in set 3
- Every trend is **increasing** except set 1, class 1, which is $-0.190 \mu eq L^{-1}$
- The increasing trends range from $0.138 \mu eq L^{-1}$ to $0.307 \mu eq L^{-1}$
- Overall sulfate is **increasing** over time
- The trends are **decreasing** from set 2 to 3, but all of set 3 is insignificant

Elevation Trends

- pH and ANC decrease as elevation increases
- Nitrate, sulfate, and SBC all increase as elevation increases
- Except for SBC all elevational trends decrease over time

Table: Dependents regressed against elevation.

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

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Data differences

Robinson 08

- 90 sites
- 11 elevation classes
- 1993 - 2002, 10 years
- includes Abrams and sites 237 and 252

Schwartz 13

- 67 sites
- 11 elevation classes
- 1993 - 2009, 17 years

Pobst 14

- 43 sites
- 6 elevation classes
- set 1: 10 years
- set 2: 6 years
- set 3: 4 years
- removed Abrams and sites 237 and 252

Results by comparison

Schwartz 13

- pH **decreased** -1.056 pH units per 1000 m gain
- ANC **decreased** -117.909 μeqL^{-1} per 1000 m gain
- insignificant **negative** trend for sulfate

Pobst 14

- pH **decreased** -0.0286 pH units per 1000 m gain
- ANC **decreased** -35.689 μeqL^{-1} per 1000 m gain
- **Positive** sulfate elevational trends **decrease** over time

Conclusions on Sulfate

sulfate desorption is of greater concern than pH levels in the park

- Lack of trend found in the Biotics effects report were attributed to high elevation soil adsorption of depositional sulfate
- Sulfate will remain absorbed to soil particles as long as soil water chemistry remains high in sulfate concentration and low in pH
- Over time most sulfate concentrations are increasing but in set 3: classes 1, 4, and 6 have negative trends
- The elevation trend is decreasing over time
- The combination of these trends support desorption of sulfate into the streams bringing the elevation trend to equilibrium

- ANOVA/Bonferroni
- Discussion

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- Power Analysis
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- A priori
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Summary

- **Water Quality is getting better**
- Sulfate sequestration is supported
- The power of the time trends are excellent
- Power analysis can help re-distribute sites
- Outlook
 - Elevation Bands
 - Effects of sulfate scrubbers

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