

Chemical changes in Virginia's brook trout streams: An analysis
of statewide surveys 1987-2010

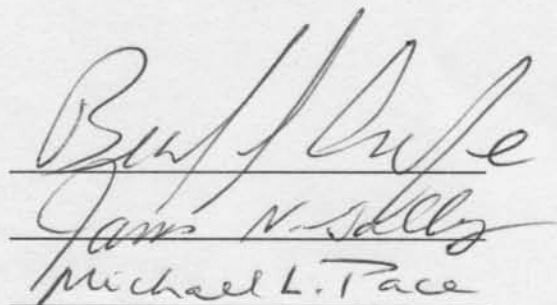
Janet Lynn Miller
New London, CT

B.A. Wesleyan University, 2003

A Thesis presented to the Graduate Faculty
of the University of Virginia in Candidacy for the Degree of Master of Science

Department of Environmental Sciences

University of Virginia
August, 2011


Buff Duse
James N. Sells
Michael L. Pace

ABSTRACT

Stream acidification, caused by atmospheric deposition of acids derived from anthropogenic emissions of SO₂ and NO_x, has major consequences for aquatic ecosystems. In response to growing environmental concerns, the United States federal government enacted a set of policies including the Clean Air Act Amendments (CAAA) of 1990 aimed at curbing emissions, which have resulted in a significant decrease in rates of acidic atmospheric deposition. This project analyzed the water chemistry of 345 of Virginia's mountain streams sampled in 1987, 2000, and 2010 to assess the long-term response of stream chemistry to decreases in atmospheric acidic deposition that resulted from emissions reductions. Between 1987 and 2010, median stream SO₄²⁻ concentration declined 18% (12.9 µeq/L) and median acid neutralizing capacity (ANC) increased 76% (44.4 µeq/L), indicating at least a partial recovery from acidification. A number of spatial, geographic, and geological characteristics were analyzed to identify factors responsible for variation in stream recovery from acidification. Stream elevation exhibited a weak but significant association with rate of recovery from acidification, with lower elevation sites showing slightly faster recovery. Although bedrock geology was significantly associated with both stream SO₄²⁻ and ANC concentrations, there was no relationship between bedrock geology and rates of recovery from acidification. Watershed area was not found to have any relationship with stream chemistry. The gypsy moth defoliation of the 1990s did not appear to affect recovery from acidification. While these geological, biological and geographical variables appear to have had little or no effect on stream chemistry, patterns of atmospheric wet

deposition suggest spatial variability in stream recovery may be driven more by differences in extrinsic input. Overall, these results suggest the mountains of Virginia are recovering from acidification and that the previously reported lagged response of streams in this region, resulting from sulfate adsorption in the soils, is now diminishing.

ACKNOWLEDGEMENTS

I would like to thank the many people who contributed to this research and made this thesis possible. First, I would like to thank my advisors, James Galloway and Jack Cosby, for their encouragement, guidance and engagement throughout this process. They were critical to the development of the project and the development of my scientific and writing skills. I would also like to thank my committee member, Michael Pace, for his constructive feedback and insights.

The data collection and analysis for this research were aided by many people and organizations over several decades. First, I would like to acknowledge all of the past and present members of the Shenandoah Watershed Study (SWAS) for their efforts in creating and maintaining this research initiative over the years. In particular I would like to Rick Webb, Suzanne Maben, and Frank Deviney who have been an integral part of the SWAS program. Their efforts to ensure the organization and coordination of the stream surveys, timely chemical analysis of the samples, and maintenance of the database have been invaluable to this project. In addition their breadth of knowledge on my research topic owing to their decades of work for SWAS was a great resource for me while completing my thesis. I would also like to thank Ami Riscassi for her help documenting some of the sampling sites prior to the survey, providing feedback to me throughout the completion of my thesis, and willingness to go on outdoor adventures with me to clear our minds.

The sampling effort required the help of many organizations and volunteers to ensure timely and accurate sample collection. Over the course of the three surveys, hundreds of people have pitched in to help. While I cannot list every

volunteer by name, I would like to acknowledge Trout Unlimited, The National Park Service, the USDA Forest Service, the EPA, and the Virginia Department of Game and Inland Fisheries for providing help with sample collection.

My acknowledgements section would not be complete without recognizing all the support I have received from family, friends, and colleagues. The Environmental Sciences Department at the University of Virginia is unique in its diversity of focus and the diversity of the background of the students. My fellow graduate students provided great feedback and ideas relating to my research, technical advice with regard to statistical methods, and moral support. These contributions were integral for the success of my graduate career, and I feel fortunate to have shared the company of such a talented group of people.

Finally, I would like to thank my family for all that they have provided over the years. My parents have always done everything in their power to provide me with opportunities for success and happiness. Their sacrifices have not gone unnoticed. My husband, Dan, has perhaps been most integral in the work of this thesis. I am fortunate to share my life with a man who is also a talented scientist. He was my in-house support with regards to the design of statistical analysis, coding of statistical tests, and also served as my informal first reader. In addition he was my biggest cheerleader and the person I could always lean on when the stress set in. I would like to acknowledge all of my family, but in particular my mom, dad, sister, and husband, for their unwavering love, support, and source of motivation. When I doubted myself, they never did.

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1. INTRODUCTION

1.1 Stream acidification and its ecosystem effects

Changes in stream chemistry can have adverse impacts on ecosystems, affecting water quality, soils, and biota (Hall et al. 1980; Lawrence et al. 1999). In particular, acidification of streams resulting from sulfur and nitrogen deposition poses a major environmental concern. Acidification of surface waters has a large impact on aquatic trophic dynamics, affecting the mortality of zooplankton, macroinvertebrates, and fish (Driscoll et al. 2003). Specifically, low pH and high levels of aluminum (which is released from terrestrial systems under conditions of chronic acid deposition and depleted base cation supply) are toxic to fish (Baker and Schofield 1982; Cronan and Schofield 1990). Fish species richness declines with decreasing pH and ANC, reflecting the loss of acid-sensitive species and their food resources (Schindler et al. 1985) in both Shenandoah National Park (Cosby et al. 2006) and the Adirondack Mountain Region (Sullivan et al. 2006). The long-term and sometimes irreversible effects of acidification on all aspects of stream ecosystems make it an urgent scientific and policy issue.

1.2. Atmospheric causes of stream acidification

Acidic atmospheric deposition, the transfer of strong acids from the atmosphere to terrestrial and aquatic ecosystems via precipitation, gases, particles, and clouds, is the primary cause of stream acidification (Driscoll et al. 2003). These acids are typically created by emissions of SO_2 , NO_x , and NH_3 (converted to NO_3^- via nitrification by microbes) from anthropogenic sources as a result of combustion of

fossil fuels, and in the case of NH_3 , agriculture. Acidic pollutants have a broad impact because they are able to affect large geographic areas, travelling great distances from their point of origin (Driscoll et al. 2001).

Charge balance in the soil and surface waters of an ecosystem assures that changes in abundance of an acidic anion such as sulfate (SO_4^{2-}) or nitrate (NO_3^-) will affect the relative abundance of other ions such as: magnesium (Mg^{2+}), potassium (K^+), calcium (Ca^{2+}), sodium (Na^+), and hydrogen (H^+). The equation for charge balance ($\mu\text{mol/L}$) is given by:

$$\begin{aligned} &2(\text{Ca}^{2+}) + 2(\text{Mg}^{2+}) + (\text{K}^+) + (\text{Na}^+) + (\text{H}^+) + 3(\text{Al}^{3+}) \\ &= 2(\text{SO}_4^{2-}) + (\text{NO}_3^-) + (\text{Cl}^-) + (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) + (\text{OH}^-) \end{aligned}$$

Soils act as a buffer against acidic deposition, providing both an exchange of base cations to neutralize the acid before it enters surface waters and removing SO_4^{2-} from solution through adsorption (Nodvin et al. 1986). Additionally, NO_3^- is removed from soils and assimilated by plants. The acid neutralizing capacity (ANC) of a system is equal to the sum of base cations minus the sum of acid anions ($\text{ANC}=\text{SBC}-\text{SAA}$); where SBC is the sum of calcium, magnesium, potassium, and sodium and SAA is the sum of sulfate, nitrate and chloride. With chronic acidic deposition, percent base saturation of soils decreases and soils are less effective in neutralizing acid inputs, leading to the subsequent acidification of soils and streams (Kirchner and Lydersen 1995).

1.3. Emissions decrease

Beginning in the 1970s, the harmful effects of acidic deposition on aquatic ecosystems and biota began to come into focus. The direct link between SO_2 and NO_x emissions and atmospheric deposition of SO_4^{2-} and NO_3^- has been well documented (e.g. Butler et al. 2001; Likens et al. 2001; Kahl et al. 2004). In 1973 U.S. emissions of SO_2 reached an all-time high, with utilities companies being responsible for 60% of the total (Driscoll et al. 2001). The documented effects of acidification on biota, such as game fisheries, and evidence for its anthropogenic cause led to increased pressure on the United States federal government to regulate emissions. Controls on emissions were first implemented by the 1970 Clean Air Act Amendments (CAAA). In 1990, congress enacted further restrictions by passing Title IV of the CAAA, with the goal of reducing acidic deposition by regulating nitrogen and sulfur emissions, primarily from utilities companies. From 1990 to 2008 there has been a national decrease of 50% in total SO_2 emissions, while national trends in NO_x emissions have shown a more moderate decline over the same time period (36%) (Figure 1) (EPA 2009).

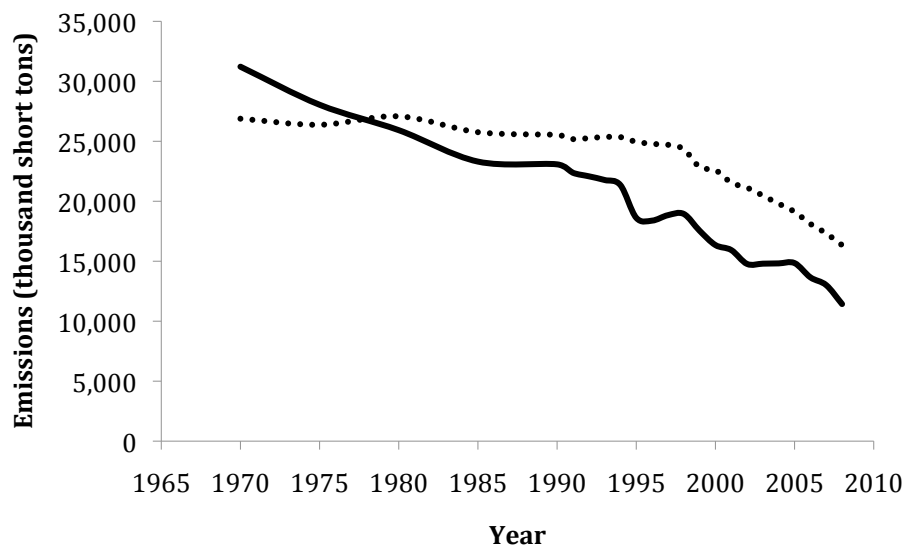


Figure 1. National trends of SO₂ (solid line) and NO_x (dashed line) emissions. Map created with data obtained from the National Emissions inventory (EPA 2009).

The decline of SO₂ and NO_x emissions has resulted in a decrease in atmospheric deposition of SO₄²⁻ and NO₃⁻ (Stoddard et al. 2003). The largest reductions have been in areas around and downwind of the Ohio River Valley, a region containing a high density of coal-fired power plants, which were a prime target of the SO₂ limitations set by the CAAA. It is apparent that policies aimed at curbing emissions have been effective in reducing acidic deposition. An important unanswered question is how aquatic systems have responded to those reductions.

1.4. Factors influencing stream response to acidification

Atmospheric deposition is divided into three categories, based on the processes by which it is formed: 1) wet deposition – the deposition of material through precipitation, 2) dry deposition – the deposition of particles and gases to

land, vegetation, or surface water, and 3) cloud deposition - the deposition of droplets of clouds and fog to land surfaces (Lovett 1994).

The susceptibility and response of streams to acidification by atmospheric deposition is influenced by many factors, including magnitude of acidic deposition, geographic location, amount of precipitation, land use, elevation, watershed area, soil composition and depth, and bedrock geology (Cosby et al. 1991; Herlihy et al. 1998; Lovett et al. 1999; Weathers et al. 2000; Sullivan et al. 2007).

Wet deposition for a given area is a function of total precipitation and its composition. Therefore, the amount of precipitation, source regions of chemical precipitates, and intensity of precipitation can impact stream chemistry (Evans et al. 2001). Atmospheric deposition, and especially dry deposition, has a variable effect with respect to amount and type of forest cover (Lovett et al. 1999). For example, it is largely assumed that coniferous forests are more effective at capturing the particles in dry deposition.

Higher elevation sites are more affected by atmospheric deposition (Lovett et al. 1999; Weathers et al. 2000). This may, in part, be the result of cloud and fog deposition which do not occur as much at lower elevation and the decreased soil-water contact time and opportunity for cation exchange on steep grades (Lovett and Kinsman 1990; Schmoyer 1990).

Bedrock also influences stream chemistry because of its ability to weather to produce acid neutralizing base cations. Streams associated with base-poor bedrock (siliciclastic) tend to be less resistant to the effects of acidic deposition than streams associated base-rich bedrock (basalt) (Cosby et al. 1991).

The composition and depth of soils, primarily produced by the weathering of bedrock, also has a strong effect on stream response to acidic atmospheric deposition. Soils are the main source of cations for neutralizing acids in most watersheds. Soils can vary in their base saturation – the proportion of soil cation exchange capacity that is occupied by exchangeable base cations – and their retention of sulfur, and therefore can have an important effect on the susceptibility of streams to acidic atmospheric deposition.

1.5. Acidic Deposition in the Mountains of Virginia

The mountains of western Virginia, part of the southern Appalachians, have one of the highest historic rates of acid deposition in the United States (Herlihy et al. 1993), making them an ideal place to study the consequences of environmental policies aimed at curbing emissions. Atmospheric sulfur deposition from coal power plants is the primary source of acidification to the streams of western Virginia (Sullivan et al. 2004). The acidification of Virginia's mountain streams has affected the viability of native brook trout populations (*Salvelinus fontinalis*), in some cases making the streams uninhabitable for this species, which is otherwise considered acid-tolerant (MacAvoy and Bulger 1995; Bulger et al. 2000).

As a result of national emissions reductions, sulfate wet deposition has declined 70% at Big Meadows, a National Atmospheric Deposition Program (NADP) station located in Shenandoah National Park (Figure 2). Although it is suggested that further reductions in emissions will be needed for most brook trout streams in

Virginia to recover (defined by an increase in ANC), some streams should be showing signs of recovery now (Webb et al. 2004).

Bedrock geology of this area mainly includes: basalt, granite, sandstone, and shale. Previous work suggests that bedrock geology exerts the strongest controls on the variability of ANC in Virginia's mountain streams, with streams in the Valley and Ridge province having lower ANC values than those in the Blue Ridge province (Cosby et al. 1991).

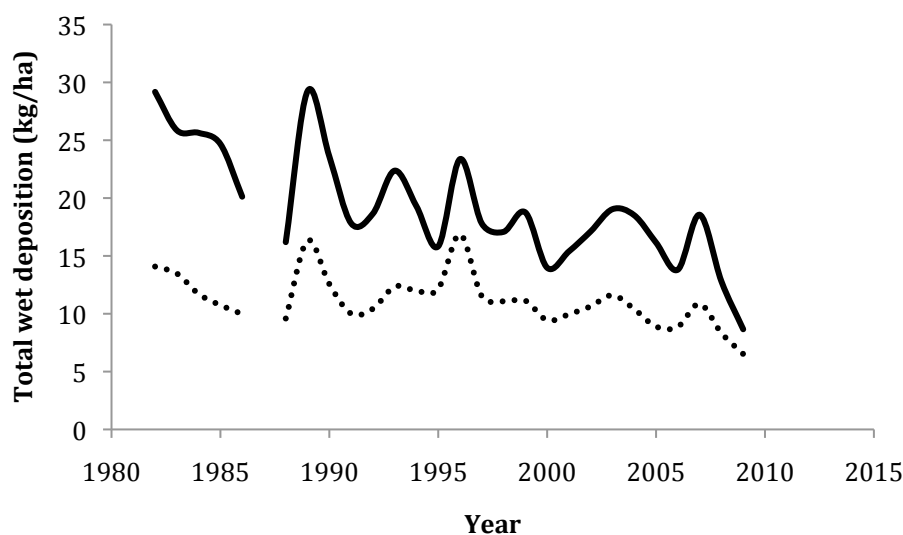


Figure 2. Total wet deposition of the ions SO_4^{2-} (solid line) and NO_3^- (dashed line) at Big Meadows, Shenandoah National Park, VA. Broken line is due to incomplete data for 1987. Map created with data obtained from the National Atmospheric Deposition Program (NADP).

Generally, NO_3^- deposition does not have as great an impact as SO_4^{2-} on stream chemistry in this region because of nearly complete uptake of nitrogen by vegetation and lower rates of NO_3^- deposition compared to SO_4^{2-} (Figure 2). Stream NO_3^- levels have been influenced by the infestation of the gypsy moth, which caused widespread defoliation in parts of Virginia in the 1990s and led to increased nitrate values

as well as other ions. Webb et al (1995) found that changes in stream chemistry associated with defoliation included increases in strong acid anions and base cations and a decrease in sulfate and ANC. The largest change in stream chemistry was in the concentration of nitrate, with concentrations increasing from pre-defoliation levels of consistently less than $5\mu\text{eq L}^{-1}$ to post-defoliation levels greater than $50\mu\text{eqL}^{-1}$ (Webb et al. 1995).

2. PROJECT OBJECTIVES AND HYPOTHESES

The goal of the this project is to analyze changes that have occurred in stream water chemistry in 345 native brook trout streams in western Virginia over the last 23 years. The focus will be on understanding the patterns of acidification and recovery in response to emissions and atmospheric deposition reductions achieved by the 1990 CAAA. For the purposes of this study, the term recovery is used to indicate an increase in ANC and/or decrease in SO_4^{2-} concentration in stream water. Three synoptic surveys of stream water composition have been performed over the past 23 years on these 345 streams. The first was in April of 1987, prior to the enactment of the CAAA of 1990. The sites were subsequently re-sampled in April of 2000 and 2010.

The main objectives of the study are: 1) to quantify the changes in concentrations stream constituents related to recovery (i.e. SO_4^{2-} , ANC) over this period and evaluate whether streams are showing signs of recovery in response to the decreases in acidic deposition achieved by emissions control legislation; 2) to determine whether elevation, watershed area, bedrock geology, climate, or

magnitude of deposition influence the rates of stream recovery; and 3) to understand the effect of gypsy moth defoliation on analysis of the response to and recovery from acidification.

These objectives are addressed by testing the hypotheses associated with 5 main questions concerning stream responses to changing acidic deposition in the mountains of western Virginia.

Question 1. Have stream SO_4^{2-} concentrations declined and ANC concentrations increased over the study period? SO_4^{2-} levels in stream water were expected to decrease while ANC increased over time for the entirety of the dataset, a trend consistent with recovery from acidification due to reduced emissions. To answer the question, the null hypothesis - that there are no significant differences in SO_4^{2-} or ANC among years - was tested.

Stream response was not expected to be consistent across all sites, therefore three main geospatial variables were tested to see if they were correlated with stream response: bedrock geology, elevation, and watershed area.

Question 2. Does bedrock geology affect the rate of recovery from acidification? Soils on basaltic bedrock have a higher base saturation than those on granitic or siliciclastic bedrock, and would therefore supply a better buffer to acidification. In addition, the rate of weathering is higher on basaltic bedrock than siliciclastic or granitic bedrock. Therefore it was expected that signs of stream recovery from acidification would vary according to bedrock geology. Because bedrock geology supplies base cations, its effect on stream chemistry was expected to be more pronounced in the recovery of ANC rather than SO_4^{2-} levels. To answer the question,

a variety of analyses were employed using both the survey dataset and bedrock dataset.

Question 3. Does elevation affect the rate of recovery from acidification?

Because higher elevation sites receive greater amounts of precipitation, and have shorter water residence times and less contact with base cation rich soil and saprolite due to the relatively steeper gradient, sites at higher elevations were expected to have a different rate of recovery from acidic deposition than sites at lower elevations. To answer the question, a variety of analyses were used to test the null hypothesis – that there are no significant differences in rate of recovery across elevations.

Question 4. Are rates of stream recovery from acidification related to

watershed area? Because the size of a watershed influences its buffering ability, watershed area was expected to influence stream response to and recovery from acidification. To answer the question, a variety of analyses were used to test the null hypothesis – that there are no significant differences in rate of recovery across magnitudes of watershed area.

Finally, in addition to the decreases in acidic deposition that occurred in the study area during the 23 years covered by the surveys, there was also a major non-atmospheric disturbance that could have affected stream water chemistry. In the early 1990's the northern part of the study area was infested by the gypsy moth. Many watersheds in the infested area suffered extensive defoliation for a number of years. While the effects of the infestation were transient, the changes in

biogeochemical cycling caused by the defoliation affected stream water chemistry for a number of years.

Question 5. Did the gypsy moth defoliation in a subset of sites affect the results of the original analysis? While the presence of gypsy moth defoliation in a subset of sample sites was expected to lead to elevated nitrate values in those sites, the impact was not expected to be so great as to drastically obscure or impede analysis of recovery from acidic deposition. To answer the question, the null hypothesis – that there are no significant differences in the rate of recovery from acidification between sites affected by the gypsy moth and sites unaffected by the gypsy moth defoliation – was tested using both stream chemistry and GIS data.

3. PROJECT METHODS

3.1 Stream Water Sample Collection

The Virginia Trout Stream Sensitivity Study (VTSSS) includes 456 sample sites located in the mountains of western Virginia (Figure. 3). These sites were chosen to be inclusive of the streams in the mountains of Virginia that support naturally reproducing brook trout, as identified by the Virginia Department of Game and Inland Fisheries (VDGIF). Some streams were excluded from VTSSS because they are underlain primarily by limestone bedrock, which makes them less susceptible to acidification. Additionally, some sites were excluded due to lack of access.

The VTSSS sites were sampled during the last week of April in 1987, 2000, and 2010 with the help of volunteers from Trout Unlimited, the National Park

and tested with a conductivity meter to ensure quality before being used for sampling.

In the field, the bottle and its cap were rinsed in the stream 3 times before collecting a 500 ml sample of stream water. Samples were then put in coolers with ice or frozen gel packs and transported back to the lab at the University of Virginia. Upon delivery to the laboratory, samples were preserved with a 0.5ml aliquot of chloroform and stored at room temperature.

3.2 Chemical Analysis of Stream Water Samples

Samples were analyzed in the SWAS laboratory at the University of Virginia. The 2010 samples were analyzed for pH and ANC on a Metrohm Titrando 809 Titration System. An 11 point method was used to calculate the Gran ANC using the following steps: 1) calculation of initial pH 2) titration of sample using 0.01 N HCl to pH of 4.5 and 4.2, recording the volume of acid added 3) addition of equal-volume aliquots of HCl in 8 steps, recording the pH and 4) titration of the sample to a pH of 3.5, recording the volume of acid added. A quality control sample (QCS) with a known pH of 4.60 was required to be within ± 0.075 pH units for a batch of samples to pass analysis. The samples collected in 1987 and 2000 were titrated manually using a 2-endpoint method (pH 4.5 and 4.3). A direct comparison of manual and automated titration methods suggests that ANC measurements differ by <3% (F.Deviney, unpublished data).

The 2010 samples were analyzed for ion (SO_4^{2-} , NO_3^- , Cl^- , Mg^{2+} , K^+ , Na^+ , Ca^{2+}) concentrations using a Dionex ICS-3000 Ion Chromatography Autosampler System

(IC). Analyses of a laboratory blank, detection limit QCS, and calibration QCS were conducted to ensure adequate performance. The data collected in 1987 and 2000 were analyzed for the anion concentrations using an older version of the IC (Dionex 14) and the cation concentrations were analyzed using an Atomic Absorption Spectrophotometer. Internal laboratory tests showed no systemic bias for the different analytical methods across characteristics (anions and cations) either overall or by ion charge (positive and negative) and biases were approximately 1 $\mu\text{eq/L}$ or less (F.Deviney, unpublished data).

3.3. Data Quality Control

Stream samples were re-analyzed if the corresponding QCS did not meet pre-defined criteria as stipulated by EPA (Paulsen 1997). Samples were also re-analyzed if they failed either or both of two additional quality control checks. First, the charge ratio (sum of acid anions divided by the sum of base cations) of each sample was calculated to verify that it was approximately equal to 1 (+/- 0.15). Second, the measured and calculated conductivities were compared to verify that they met the similarity criteria described by Paulsen (1997). Samples that deviated from these expectations required reanalysis.

3.4. Overview of datasets

The primary dataset contains results from the 3 surveys (1987, 2000 and 2010) and includes: pH, ANC, ion concentrations (SO_4^{2-} , NO_3^- , Cl^- , Mg^{2+} , K^+ , Na^+ , Ca^{2+}), sampling site geographic coordinates, and sampling site elevation. Sites were

removed if they were known to have been limed based on information from Virginia's Department of Game and Inland Fisheries (VDGIF). Additionally, two sites (SY21 and BO01) were removed because of abnormally high sulfate values, suggesting an additional source of sulfur to the system. Lastly, only sites sampled in all 3 survey years were included in the analysis. The final dataset contained 345 sites.

Additional datasets were obtained to provide geographical, geological and environmental information for each sampling site. The bedrock lithology classification scheme that was completed as part of the Southern Appalachian Mountain Initiative (SAMI) was used to obtain site-specific bedrock geology data (Sullivan et al. 2007). This dataset specifies the percentage of each major lithological class (siliceous, argillaceous, felsic, mafic, and carbonate) by watershed. For the purposes of this project, felsic will be referred to as granitic and mafic will be referred to as basaltic. Additionally, siliceous and argillaceous were combined to create a siliciclastic bedrock lithology classification.

Site-specific elevation was calculated using topographic map interpolation. Watershed area was calculated with GIS using a shapefile with newly delineated watersheds provided by the Clean Air Markets Division (CAMD) of EPA. In addition, Virginia's Department of Forestry provided a GIS shapefile summarizing the cumulative extent of gypsy moth defoliation in our study area through 2007. This file was used to identify which sites were affected by the gypsy moth infestation. Palmer drought indices from the National Climatic Data Center (NCDC) were used to evaluate potential differences in climate among the sample years. Information on

atmospheric sulfur and nitrogen deposition data was obtained from the National Atmospheric Deposition Program (NADP), and then converted to site-specific deposition by CAMD (Grimm and Lynch 2004).

3.5. Statistical Analysis

All statistical analysis were performed in software package R version. 2.9.2 (open source) on the 345 sites described above unless otherwise indicated.

Different statistical techniques and analysis designs were used to address each of the five main questions concerning stream responses to changing acidic deposition.

Question 1. Have stream SO_4^{2-} concentrations declined and ANC concentrations increased over the study period? Analysis of variance (ANOVA) was used to test the null hypothesis - that there are no significant differences in SO_4^{2-} or ANC concentrations in streams among the 3 survey sampling periods. Sulfate and ANC values were transformed to conform to assumptions of normality. Sulfate values were log transformed and ANC was also log transformed after adding 20 to each value. Separate ANOVAs were run with either SO_4^{2-} or ANC as the dependent variable and with sampling year as the independent variable. For each ANOVA, a Tukey's *post hoc* comparison test was performed to determine which years were significantly different from each other. Spatial autocorrelation can represent an important form of pseudoreplication (Sokal and Rohlf 1995). Mantel tests found that both SO_4^{2-} and ANC were spatially autocorrelated ($p < 0.05$). Therefore, the effective sample size (and corresponding degrees of freedom) for each ANOVA were

adjusted using the Fortin and Dale (2005) correction. In all cases the correction did not qualitatively change the results so uncorrected degrees of freedom are reported.

Question 2. Does bedrock geology affect the rate of recovery from acidification?

To test the null hypothesis that bedrock geology had no significant effect on SO_4^{2-} or ANC values over time, multiple statistical methods were used. The bedrock geology dataset provided percent watershed cover in 5 lithology classes as described above. Siliceous and argillaceous were combined to form a siliciclastic lithology group, and carbonate is not a substantial component of the bedrock in the study area, leaving 3 main bedrock classes: siliciclastic, basaltic and granitic. First, analyses using the bedrock classes as continuous variables were run. A total of 6 simple linear regressions with each bedrock type as the independent variable and change in either SO_4^{2-} or ANC as the dependent variable were conducted. Second, analysis of covariance (ANCOVA) with sampling year as the categorical independent variable, the log transformed SO_4^{2-} or ANC values as the dependent variable, and the 3 main bedrock classes as covariates was used to further investigate the relationship between bedrock and stream chemistry. The datasets were tested to verify that they met the assumptions of ANCOVA. Finally, 2-way ANOVAs with sampling year and bedrock geology as independent variables and either SO_4^{2-} concentration or ANC as the dependent variable were performed. To convert bedrock geology into a categorical variable for these 2-way ANOVAs, each site was assigned to a bedrock class based on a threshold composition of 95% homogeneity. Sites without 95% of one lithology were grouped into a heterogeneous category. When the result of the

overall ANOVA model was significant ($p < 0.05$), a Tukey's *post hoc* comparison test was used to determine which bedrock geologies were significantly different from each other.

Question 3. Does elevation affect the rate of recovery from acidification? To test the null hypothesis that there were no significant differences in SO_4^{2-} or ANC values over time across elevations, two different types of analyses were employed. First, the ANOVA from the original analysis testing for differences in SO_4^{2-} or ANC among years was repeated using sample site elevation as a covariate, making it an ANCOVA. Second, site elevation was regressed against change in either SO_4^{2-} or ANC (derived, continuous variable) between 1987 and 2010. These analyses were performed in terms of both absolute and proportional change between 1987 and 2010. Assumptions of linear regression were tested and satisfied prior to analysis.

Question 4. Are rates of stream recovery from acidification related to watershed area? To test the null hypothesis that there were no significant differences in SO_4^{2-} or ANC values over time across watershed area, the ANCOVA and regression analysis described directly above was repeated after substituting watershed area (a continuous variable) for elevation.

Question 5. Did the gypsy moth defoliation in a subset of sites affect the results of the original analysis? To test the null hypothesis that there were no significant differences between sites affected by the gypsy moth defoliation and sites

unaffected by the gypsy moth defoliation in SO_4^{2-} or ANC values over time, a 2-way ANOVA was used. Using a shapefile from the Virginia Department of Forestry that shows the extent of gypsy moth defoliation in Virginia, the subset of sites affected by the gypsy moth using ESRI ArcMap v. 9.3.1 were identified. Approximately 70% of the study sites (241 of 345) were affected by the gypsy moth. This information was used to create a presence/absence categorical variable to indicate whether each site was affected by the gypsy moth defoliation. In the 2-way ANOVA, the independent variables were sampling year and the presence/absence of gypsy moth defoliation. The dependent variable was either SO_4^{2-} or ANC. Using a 2-way ANOVA also allowed me to investigate whether there was an interaction between sampling year and the presence/absence of gypsy moth.

4. RESULTS

4.1. Changes in Stream Chemistry Among Years

The null hypothesis, that there are no significant differences in SO_4^{2-} or ANC concentrations in streams among the 3 survey sampling periods, was rejected by the statistical analyses. The sampling years differed significantly for both SO_4^{2-} (ANOVA, $F_{df=2,1038}=9.29$, $p < 0.001$) and ANC (ANOVA, $F_{df=2,1038}=31.6$, $p < 0.001$). Tukey's tests showed that the 2010 SO_4^{2-} concentrations were significantly different from both 1987 and 2000, but that 1987 and 2000 were not significantly different from each other (Figure 4). In contrast, all three sampling years were significantly different from each other with respect to ANC (Figure 5).

Median stream SO_4^{2-} concentrations have declined by 18% (12.9 $\mu\text{eq/L}$) and median ANC has increased by 76% (44.4 $\mu\text{eq/L}$) in the mountains of Virginia since the initial survey was conducted in 1987, a substantial improvement in overall water quality (Table 1).

Table 1. Median values (raw data) of SO_4^{2-} and ANC in the 345 survey sites used for analysis.

Year	SO_4^{2-} ($\mu\text{eq/L}$)	ANC ($\mu\text{eq/L}$)
1987	71	58
2000	67.3	66.9
2010	58.2	102.4

There was a wide range in the magnitude and direction of response among stream sites; however, the vast majority of sites showed signs of recovery. The median of the ANC slopes of all sites was 1.72 $\mu\text{eq/L/year}$ (min=-11.5, max=57, sd=5.2) and 96% of sites had a slope greater than zero. Likewise, the majority of sites had a decreasing trend in SO_4^{2-} over time (80%) with a median slope of -0.52 $\mu\text{eq/L/year}$ (min=-6.0, max=5.38, sd=0.86).

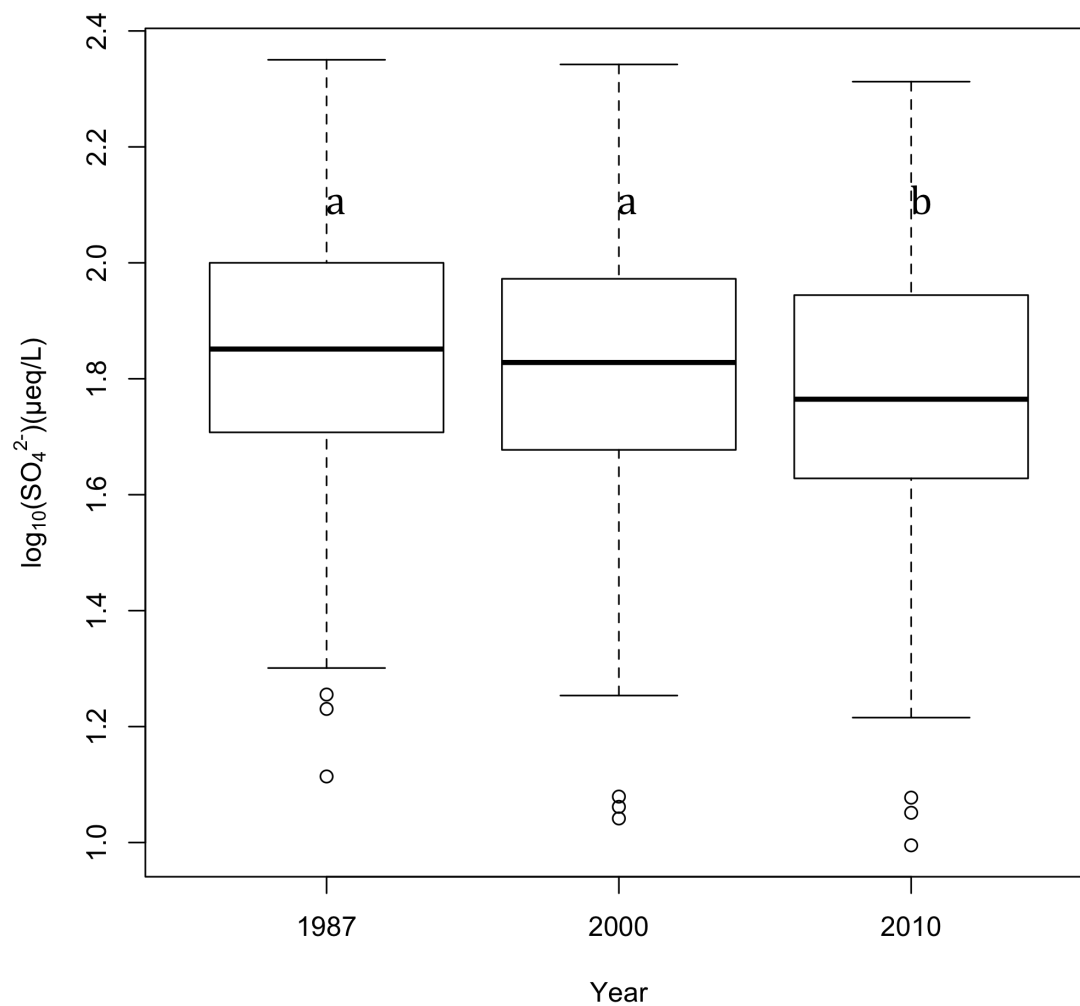


Figure 4. Box plot of log transformed SO_4^{2-} values for 1987, 2000 and 2010. Bold horizontal lines represent medians and horizontal lines of the box indicate 25th and 75th percentiles. Whiskers are minimum and maximum or 1.5 times the interquartile range (whichever is smaller). Letters indicate significant differences among years based on a Tukey's test. Open circles indicate outliers.

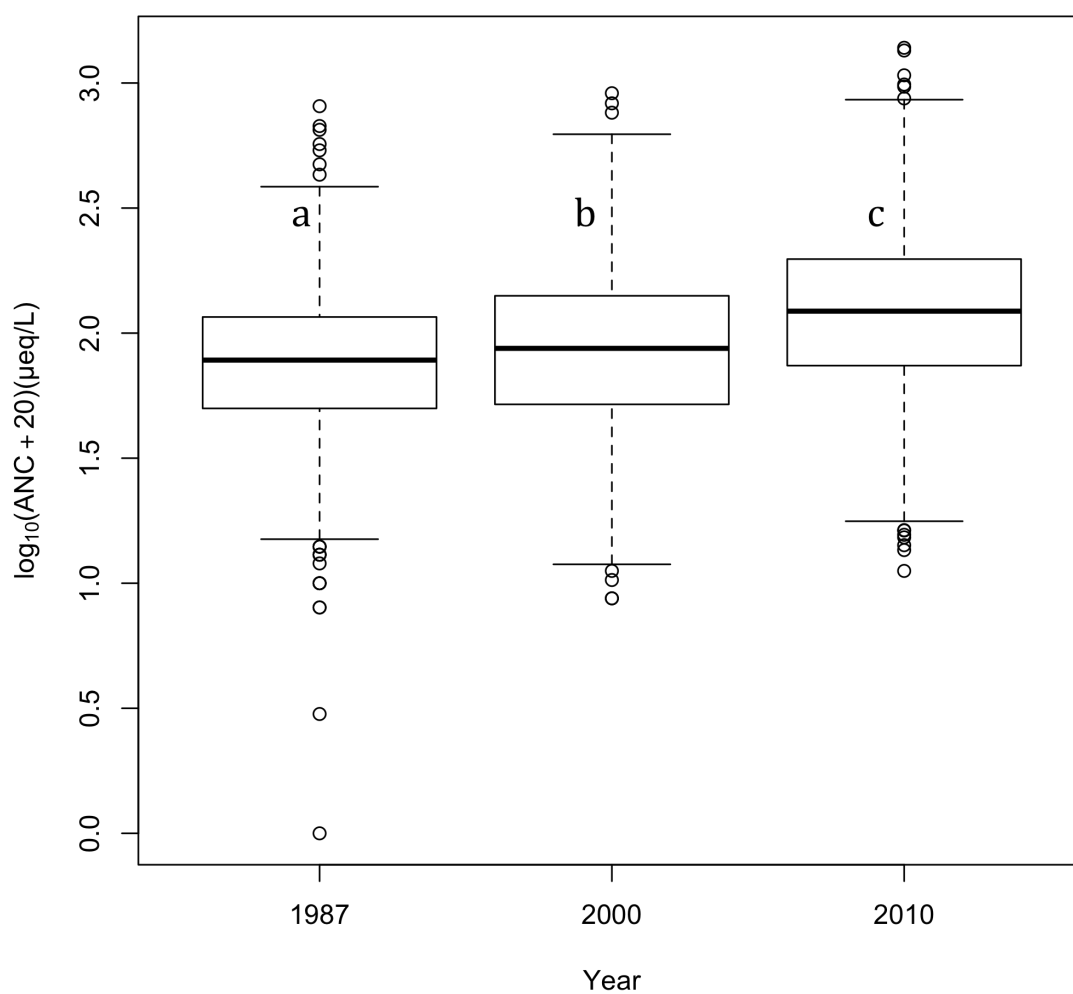


Figure 5. Box plot of log transformed ANC values for 1987, 2000 and 2010. Bold horizontal lines represent medians and horizontal lines of the box indicate 25th and 75th percentiles. Whiskers are minimum and maximum or 1.5 times the interquartile range (whichever is smaller). Letters indicate significant differences among years based on a Tukey's test. Open circles indicate outliers.

4.2. Influence of Geological and Geographical Variables on Stream

Chemistry

Bedrock Effects

The null hypotheses, that bedrock geology had no significant effect on SO_4^{2-} or ANC values over time, was accepted. Multiple analyses of the effect of bedrock geology on the recovery of brook trout streams from acidification were undertaken.

The six linear regressions relating bedrock geology classes to change (2010-1987) in either SO_4^{2-} or ANC were not significant (Table 2).

Table 2. Results of linear regressions between bedrock and change in SO_4^{2-} or ANC concentrations.

Independent Variable	Dependent Variable	R²	P	Equation
Granitic	Change in ANC (2010-1987)	0.008274	0.04996	$Y = 80.52 - 0.3124X$
Granitic	Change in SO_4^{2-} (2010-1987)	0	0.9582	$Y = -12.92 - 0.001X$
Basaltic	Change in ANC (2010-1987)	0.0003417	0.7323	$Y = 71.20 + 0.1007X$
Basaltic	Change in SO_4^{2-} (2010-1987)	0.007295	0.1133	$Y = -12.4 - 0.075X$
Siliciclastic	Change in ANC (2010-1987)	0.009385	0.07232	$Y = 55.11 + 0.2658X$
Siliciclastic	Change in SO_4^{2-} (2010-1987)	0.001087	0.5416	$Y = -13.9 + 0.014X$

Despite the undetectable effect of bedrock geology on stream recovery from acidification, there were noteworthy results regarding the influence of bedrock geology on the magnitudes of the concentrations of SO_4^{2-} and ANC. ANCOVA was used as an alternative method to linear regression to investigate whether there was a relationship between bedrock and stream chemistry. The ANCOVAs (using SO_4^{2-} or ANC) showed all 3 bedrock geologies (siliciclastic, granitic, and basaltic) had a statistically significant effect on concentration (Tables 3, 4). However, the

interaction terms with year were not significant and suggest that while the magnitudes of SO_4^{2-} or ANC might be related to geology, the rate of recovery is not significantly different among different bedrock geologies.

Table 3. Results of ANCOVA, testing the effect of year and bedrock geology on log transformed sulfate values.

dependent variable: $\log_{10}(\text{SO}_4^{2-})$

Source	df	Sum of Squares	Mean Square	F	P
Year	2	1.009	0.504	12.3011	5.27E-06
Silic	1	9.5	9.5	231.7429	< 2.2e-16
Gran	1	1.635	1.635	39.8771	4.04E-10
Basalt	1	0.873	0.873	21.2864	4.46E-06
Year*Silic	2	0.138	0.069	1.6886	0.185305
Year*Gran	2	0.021	0.011	0.2566	0.773757
Silic*Gran	1	0.278	0.278	6.7708	0.009402
Year*Basalt	2	0.01	0.005	0.1272	0.880566
Silic*Basalt	1	0.003	0.003	0.0632	0.801617
Gran*Basalt	1	1.818	1.818	44.3418	4.52E-11
Year*Silic*Gran	2	0.039	0.019	0.4738	0.622747
Year*Silic*Basalt	2	0.003	0.002	0.0416	0.959217
Year*Gran*Basalt	2	0.008	0.004	0.1033	0.901838
Silic*Gran*Basalt	1	0.253	0.253	6.161	0.013222
Year*Silic*Gran*Basalt	2	0.002	0.001	0.021	0.979264
Residuals	1011	41.444	0.041		

Table 4. Results of ANCOVA, testing the effect of year and bedrock geology on log transformed ANC values.

dependent variable: $\log_{10}(\text{ANC}+20)$

Source	df	Sum of Squares	Mean Square	F	P
Year	2	8.389	4.194	36.5918	4.54E-16
Silic	1	11.282	11.282	98.425	< 2.2e-16
Gran	1	5.43	5.43	47.3675	1.031E-11
Basalt	1	1.208	1.208	10.5422	0.001205
Year*Silic	2	0.281	0.141	1.2259	0.293943
Year*Gran	2	0.037	0.019	0.1633	0.849361
Silic*Gran	1	0.955	0.955	8.3338	0.003974
Year*Basalt	2	0.353	0.177	1.541	0.214678
Silic*Basalt	1	0.0004185	0.0004185	0.0037	0.951833
Gran*Basalt	1	1.065	1.065	9.287	0.002368
Year*Silic*Gran	2	0.071	0.036	0.3117	0.732282
Year*Silic*Basalt	2	0.016	0.008	0.0677	0.934532
Year*Gran*Basalt	2	0.011	0.005	0.0469	0.954212
Silic*Gran*Basalt	1	0.243	0.243	2.1237	0.145349
Year*Silic*Gran*Basalt	2	0.018	0.009	0.0805	0.922632
Residuals	1011	115.89	0.115		

Lastly the 2-way ANOVAs, with year and bedrock geology as independent variables and SO_4^{2-} concentration or ANC as the dependent variable were used as an alternative to ANCOVA and linear regression and showed significant differences among bedrock classes. However in all instances there was no significant interaction between year and bedrock geology, so that term was removed from the models. Sample sizes for each bedrock class were substantially different, with basaltic bedrock having the smallest sample size (7), siliciclastic with the largest (185) and heterogeneous (89) and granitic (64) falling in the middle.

A 2-way ANOVA identified a significant effect of both sampling year ($F_{df=2,1029}=12.151, p<0.001$) and bedrock geology class ($F_{df=3,1029}=106.989, p=0.001$) on SO_4^{2-} concentration. A Tukey's test showed that all pairwise comparisons of the

SO_4^{2-} values for the bedrock classes were significant except for the comparison between basaltic bedrock sites and those with heterogeneous bedrock. Mean SO_4^{2-} concentrations for all bedrock classes declined across time, and the sites underlain by siliciclastic bedrock had the highest mean SO_4^{2-} concentration for each year and sites underlain by granitic bedrock had the lowest mean SO_4^{2-} concentration for each year (Figure 6A).

ANC also differed significantly among years (ANOVA: $F_{df=2,1029}=35.48$, $p<0.001$) and among bedrock geology classes (ANOVA: $F_{df=3,1029}=42.85$, $p<0.001$). A Tukey's test showed that all pairwise comparisons of the ANC values for the bedrock classes were significant except for the comparison between basaltic bedrock sites and those with heterogeneous bedrock. Mean ANC increased across time for all bedrock classes and sites underlain by basaltic bedrock had the highest mean ANC for each year while sites underlain by siliciclastic bedrock had the lowest mean ANC for each year (Figure 6B).

Overall, these analyses point to the same conclusion that bedrock geology is significantly related to stream acidity, but not to the observed recovery from acidification over the 23 year sampling period.

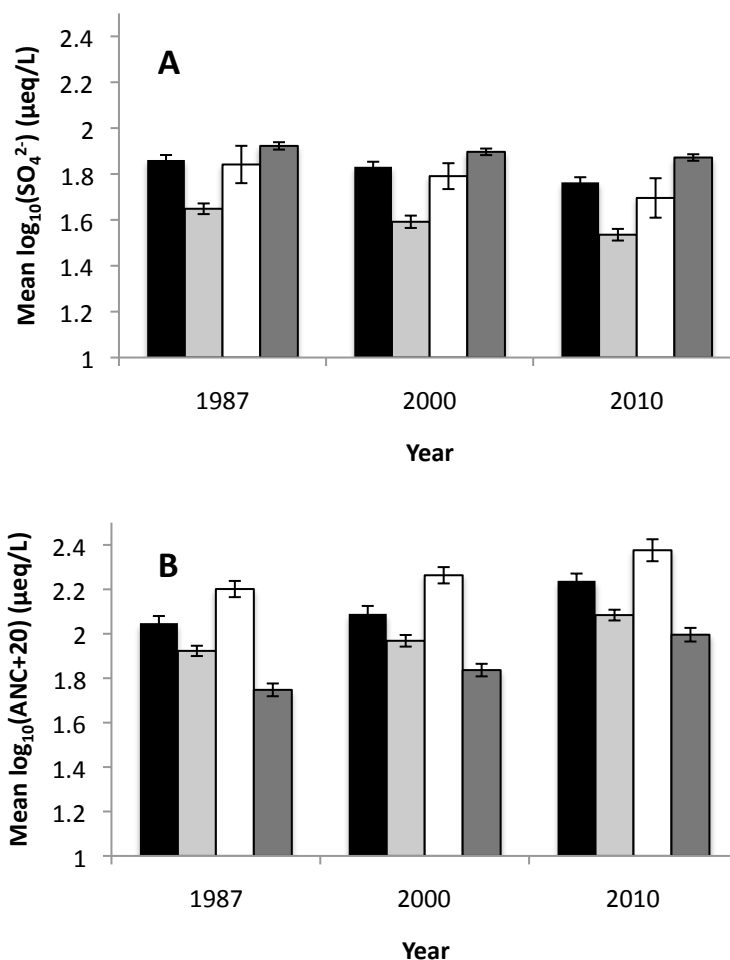


Figure 6. Mean values of log transformed values of SO_4^{2-} (A) and ANC (B) by year and broken down by 95% homogeneous bedrock classes: heterogeneous (black), granitic (light gray), basaltic (white), siliciclastic (dark gray). Error bars represent standard error of the mean.

Elevation Effects

Analyses were performed to test the null hypothesis - that there were no significant differences in SO_4^{2-} or ANC values over time across elevations. The ANCOVAs used to examine the relationship between either SO_4^{2-} concentration or ANC and year and elevation, showed no relationship between elevation of stream recovery from acidification. The interaction terms between elevation and year were

not statistically significant, and therefore the interaction term was removed from the model. The ANCOVA showed significant effects of year ($F_{df=2,1031}=9.67$, $p < 0.001$) and site elevation ($F_{df=1,1031}=44.09$, $p < 0.001$) on SO_4^{2-} concentrations. A second ANCOVA also showed significant effects of year ($F_{df=2,1031}=34.31$, $p < 0.001$) and site elevation ($F_{df=1,1031}=88.60$, $p < 0.001$) on ANC.

The relationships between change in SO_4^{2-} concentration or ANC and elevation were all very weak but significant. The regression analysis of elevation versus change in SO_4^{2-} had the highest R^2 value (0.11) of all the iterations (Figure 7). The positive slope between elevation and change in SO_4^{2-} , suggests decreases in SO_4^{2-} from 1987 to 2010 are greater at low elevations and closer to zero at high elevations (Figure 7). The relationship between elevation and proportional change in SO_4^{2-} had a lower R^2 (0.03) and p value (0.001), making it a weaker relationship that explained little of the variance in the data.

The relationship between elevation and ANC was weaker and less significant than that of elevation and SO_4^{2-} . When using change in ANC as the dependent variable, the $R^2 = 0.016$ and $p=0.02$, suggesting elevation explained very little of the variance in change in ANC. The results of the linear regression between elevation and proportional change in ANC was not significant ($R^2=0.000007$, $p= 0.9$).

Watershed Area

While the analyses using elevation as the independent variable showed weak but significant relationships, the relationships between watershed area and change in SO_4^{2-} or ANC were even weaker and not significant for both the regressions and ANCOVA. Therefore the null hypothesis, that there were no significant differences in SO_4^{2-} or ANC values over time across watershed area, was accepted.

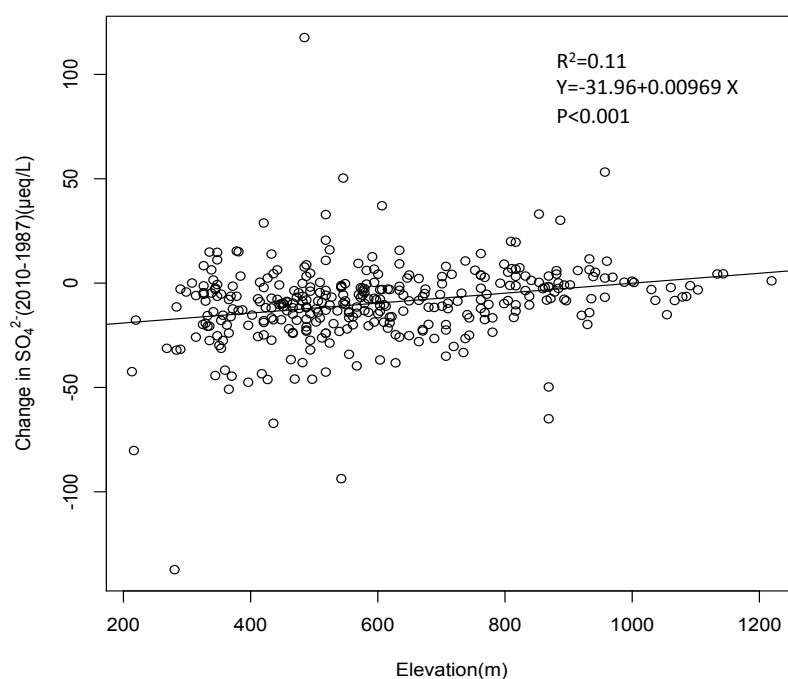


Figure 7. Regression of site elevation (meters) versus change in SO_4^{2-} between 1987 and 2000 for 345 streams.

4.3. The Effect of Gypsy Moth Defoliation on Observed Changes in Stream Chemistry

The null hypothesis, that there were no significant differences between sites affected by the gypsy moth defoliation and sites unaffected by the gypsy moth defoliation in SO_4^{2-} or ANC values over time, was tested and accepted. Gypsy moth defoliation and year were significantly associated with SO_4^{2-} levels (2-way ANOVA; Year: $F_{df=2,1029}=9.55$, $p<0.001$; Gypsy moth: $F_{df=1,1029}=27.27$, $p<0.001$), but there was no significant interaction between gypsy moth defoliation and year ($F_{df=2,1029}=2.37$, $p=0.09$), indicating that defoliation did not have a substantial effect on recovery from acidification. Sites with a history of defoliation had significantly higher SO_4^{2-} levels (69.5 $\mu\text{eq/L}$) than unaffected sites (57.7 $\mu\text{eq/L}$). Neither gypsy moth defoliation nor the interaction between gypsy moth defoliation and year were significantly associated with ANC, which further confirms that defoliation did not have a significant effect on stream chemistry.

Sites affected by gypsy moth defoliation showed a steady decline in SO_4^{2-} with time while sites without the gypsy moth show a slight increase in the 2000 sample (Figure 8A). Mean ANC values for each of the 3 years show near identical values for 2000 and 2010, and a slightly higher mean ANC for the sites without gypsy moth defoliation (Figure 8B).

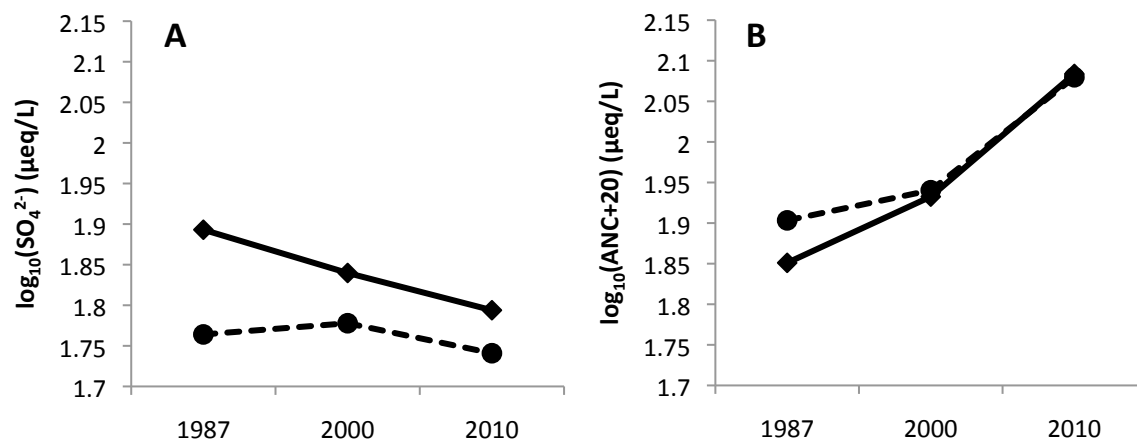


Figure 8. Logarithmic mean values for SO_4^{2-} and ANC for each of the 3 sample years for sites with gypsy moth defoliation (solid line) and sites unaffected by gypsy moth defoliation (dashed line).

5. DISCUSSION

5.1. Temporal variation in stream chemistry

The primary finding of this 23-year study is that there have been significant changes in SO_4^{2-} and ANC in Virginia's mountain streams over time. The 3 sample periods show that SO_4^{2-} is declining with time and ANC is increasing with time across the 345 study sites, a trend consistent with the recovery from acidification. These changes in stream chemistry from 1987 to 2010 correspond to an increase in the percentage of streams now considered suitable habitat for brook trout habitat based on the classification reported by Bulger et al. (2000). Whereas only 55% of Virginia streams were classified as suitable in 1987, that number has now risen to 77%. While decreased acidic atmospheric deposition is likely a primary driver of these signs of stream recovery, there are other environmental variables that could be influencing response.

5.2. Temporal climate variability

Variability in weather patterns among the 3 sampling years could be an explanation for the observed pattern in recovery. For instance, if each subsequent sampling year received more precipitation input it could lead to the dilution of analytes such as SO_4^{2-} , which would be manifested as a downward trend. While the weather patterns were not constant in the three sample periods, the observed weather patterns do not suggest that the variation in climate enhanced the result of recovery. Climate, and specifically precipitation is known to affect ion concentrations in stream water (Evans et al. 2001). Palmer drought indices for the study area for the month of April indicate that overall 1987 and 2010 were wetter years in comparison to 2000 (Figure 9). It is often assumed that Cl^- is conservative with respect to hydrology in the sense that sources and sinks are negligible compared to inputs and outputs (Lovett et al. 2005), and that drought years would produce lower yield and lead to the evapoconcentration of Cl^- . Therefore, we would expect to see increased Cl^- concentrations in 2000 as compared to 1987 and 2010 if drought was affecting stream chemistry. However, the data show that median Cl^- concentrations were the lowest in 1987 (18 $\mu\text{eq/L}$) and essentially equal in 2000 and 2010 (20.5 $\mu\text{eq/L}$ and 20.4 $\mu\text{eq/L}$, respectively). Furthermore, from a statistical standpoint, Cl^- concentrations in the 2000 and 2010 were not significantly different from each other, a result inconsistent with expectations of a climatic effect on stream chemistry (Figure 10). Finally, because we find a unidirectional downward trend in sulfate, but no unidirectional trend in weather patterns or chloride, it is

unlikely that variability in weather influenced the finding of stream recovery from acidification.

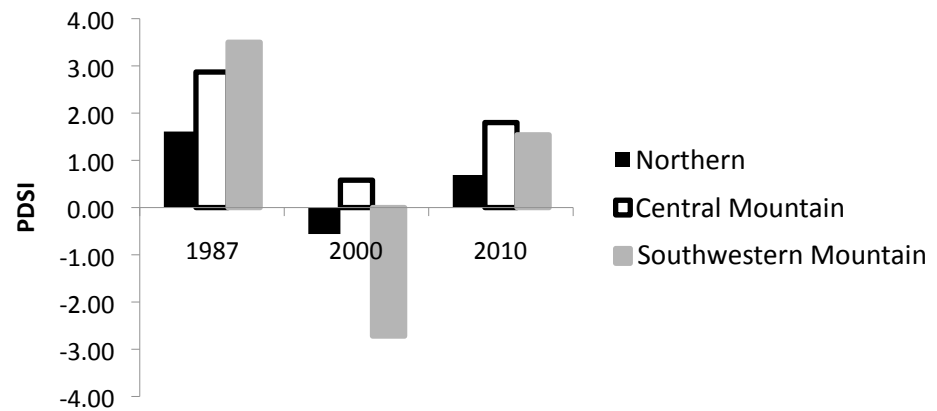


Figure 9. Palmer Drought Indices (PDSI) for April for the Northern(4), Central Mountain (5), and Southwestern Mountain (6) regions of Virginia (negative numbers indicate drought conditions). Data obtained from the National Climatic Data Center (NCDC).

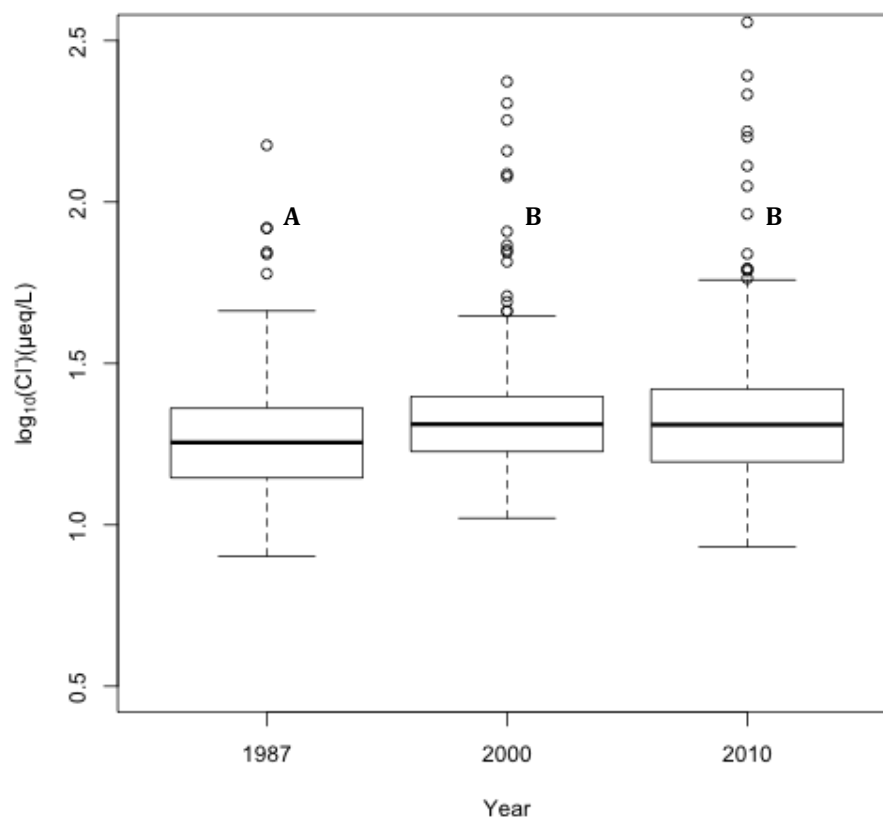


Figure 10. Box and whisker plot of log transformed Cl^- for the three study years (ANOVA: $F_{df=2,1032}=12.00$, $p < 0.001$). Bold horizontal lines represent medians and horizontal lines of the box indicate 25th and 75th percentiles. Whiskers are minimum and maximum or 1.5 times the interquartile range (whichever is smaller). Letters indicate significant differences among years based on a Tukey's test. Open circles represent outliers.

5.3. Effect of sampling scheme on observed temporal variation

Because this analysis investigates changes in stream chemistry over a 23-year period but with sampling in only 3 of those years, it is possible that one or more of the sampling years may have biased the estimated rates of stream recovery from acidification. The availability of data from a more frequent sampling of a subset of 65 of the survey sites may provide insight into this possibility. The

observed rate of recovery could be exaggerated by calculating the slope through 3 points in time rather than 23 points. To illustrate this point, consider the regression plots in Figure 11 which show the median ANC and SO_4^{2-} for the quarterly sites ($n=65$) for all 23 years. Drawing the trend lines through the 3 survey years yields a slope approximately twice as steep as the slope of the trend line drawn through all 23 points (Figure 11). While both the 3-year and 23-year dataset show the same trend direction, the 3-year dataset gives a much higher estimate of the rate of recovery.

The differences in magnitudes of the trends between the 3 year and 23 year regressions further suggests that one or more of the 3 years in the survey dataset could be an outlier. For example; based on data collected from the subset of sites in April of each of the last 23 years, the year 2010 had the lowest median SO_4^{2-} concentration and highest median ANC on record for the 23-year study period (Figure 12). These potential outliers are even more exaggerated when the survey data ($n=345$) for 1987, 2000, and 2010 are inserted into the plots (Figure 13). While the slope of the quarterly data medians drawn through 3 points in time yields a higher magnitude of recovery than the slope of the same data through 23 points in time gives credence to the possibility that our result may be exaggerated by selection of years, it does not directly address the anomalous values seen in 2010.

Was 2010 an outlier year, or is it the year the southeast region of the United States begins to really turn a corner and show signs of recovery from the previous decades of acidic atmospheric deposition? Kahl et al. (2004) showed that the streams in the Blue Ridge are recovering at a much slower rate than those in the

northern Appalachian from 1990-2000, and SO_4^{2-} and ANC appeared to actually be trending in the opposite direction of recovery. Recovery from years of acidification can be hindered both by the loss of base cations from soils due to prolonged exposure to acidic deposition and their slow replacement as well as sulfate adsorption by soil (Galloway et al. 1983; Cosby et al. 1985; Likens et al. 1996). One of the main reasons that the southeast is believed to be recovering more slowly than the northeast is that the southeast has older soils with greater clay content and therefore has a greater capacity for sulfate adsorption (Galloway et al. 1983; Elwood 1991). Therefore, our result of dramatically lower stream sulfate values in the 2010 year could be the first sign that sulfate adsorption is no longer hampering recovery, a hypothesis that can be confirmed with future years of monitoring.

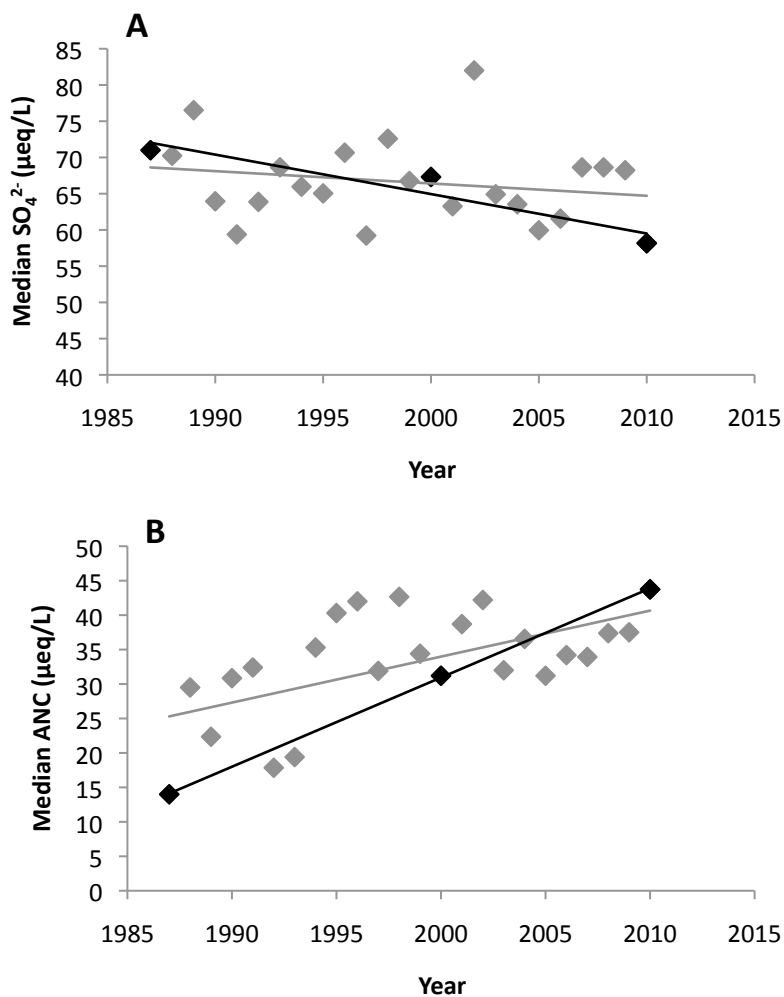


Figure 11. Scatter plots of median SO_4^{2-} (A) and ANC (B) for the quarterly dataset. Gray line indicates the best-fit line through all 23 points in time. Black line indicates best-fit line drawn through 1987, 2000, and 2010.

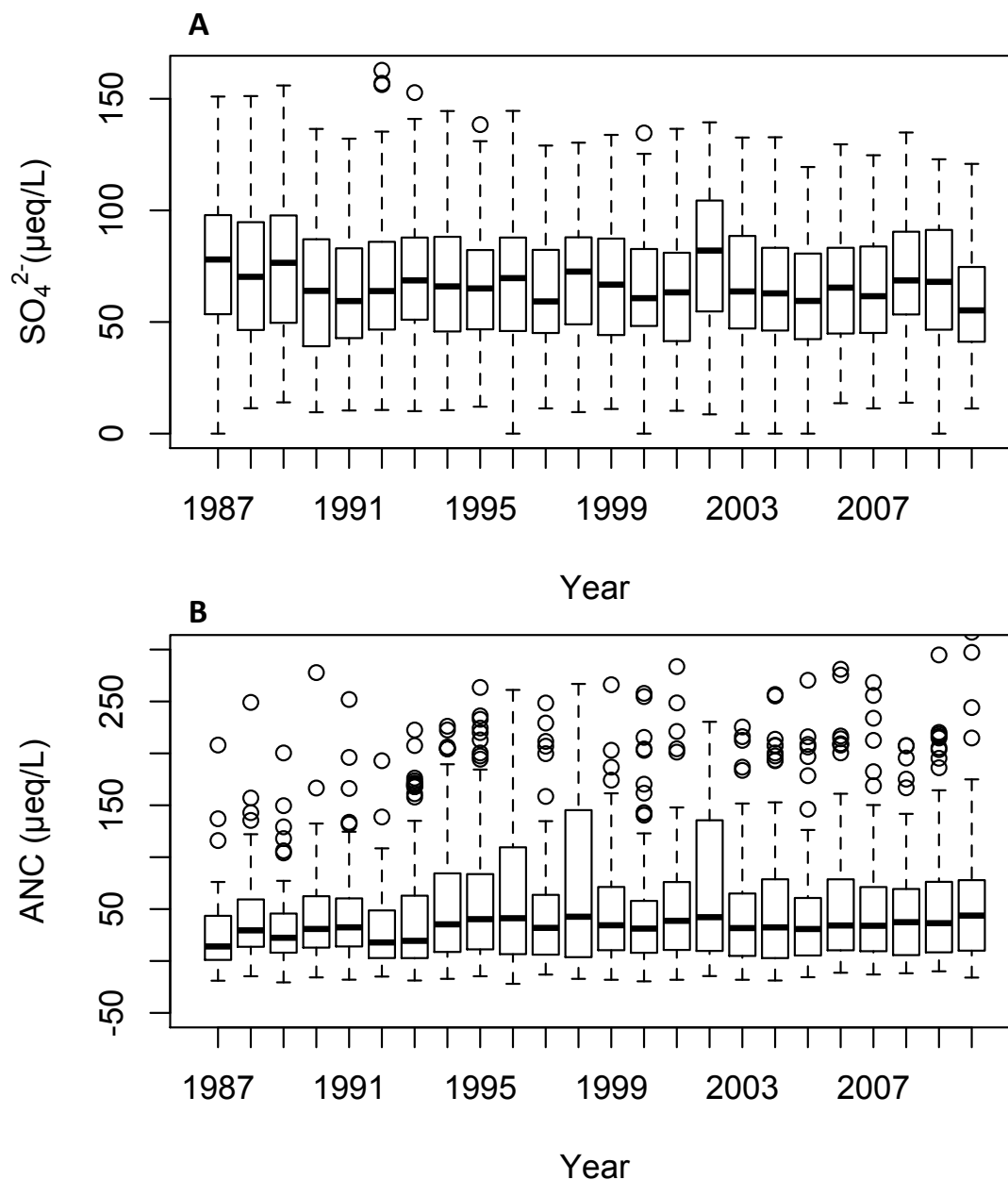


Figure 12. Box and whisker plots of sulfate (A) and ANC (B) for the April sampling period using data from the quarterly sites ($n=65$) which are a subset of the survey sites. Bold horizontal lines represent medians and horizontal lines of the box indicate 25th and 75th percentiles. Whiskers are minimum and maximum or 1.5 times the interquartile range (whichever is smaller).

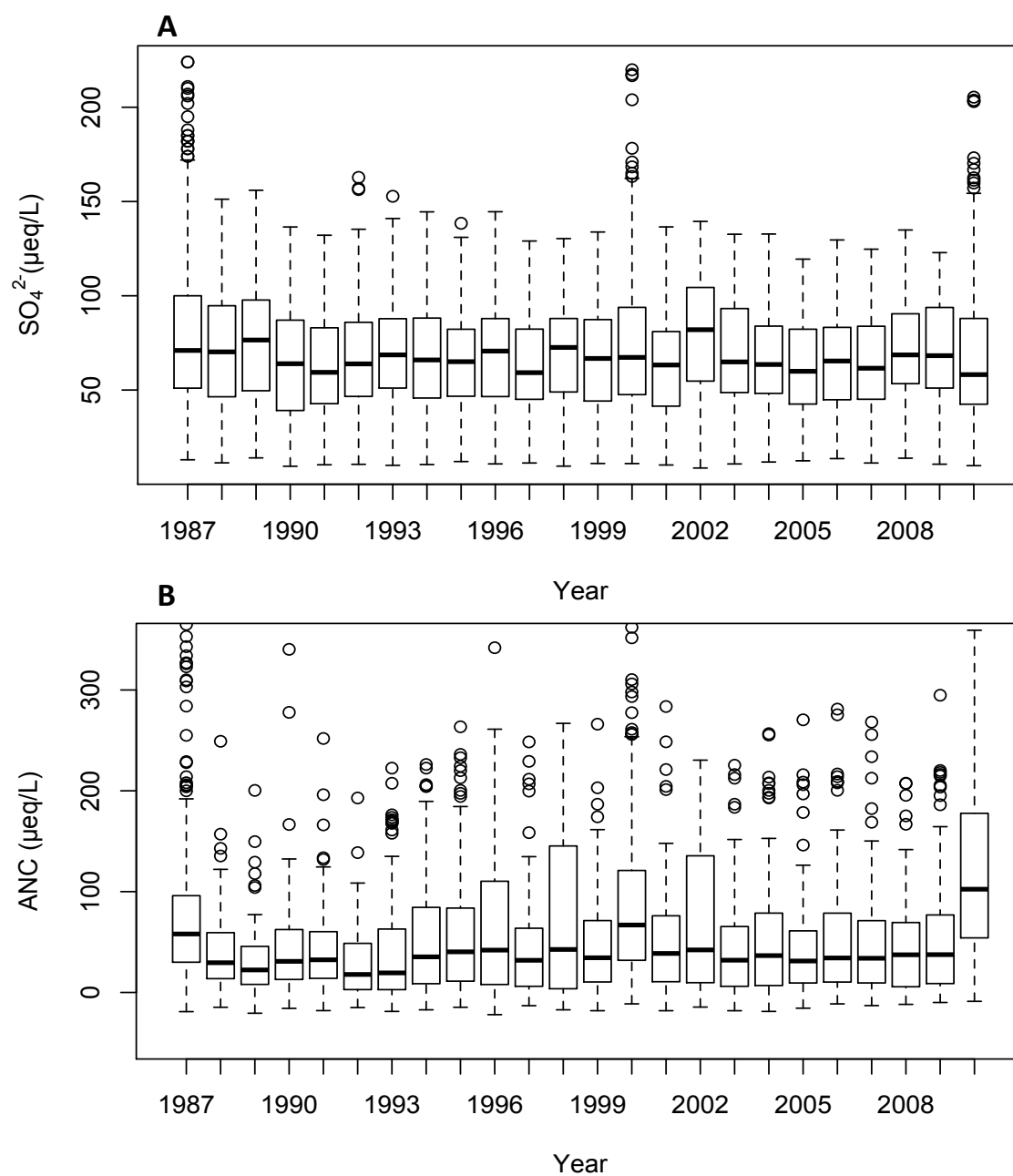


Figure 13. Box and whisker plots of sulfate (A) and ANC (B) for the April sampling period. The years 1987, 2000 and 2010 use data from the survey sites ($n=345$) and the remaining years use data from the quarterly sites ($n=65$) which are a subset of the survey sites. Bold horizontal lines represent medians and horizontal lines of the box indicate 25th and 75th percentiles. Whiskers are minimum and maximum or 1.5 times the interquartile range (whichever is smaller).

5.4. Spatial variation in stream chemistry

While stream recovery from acidification seems correlated with time, there is still a lot of unexplained variance in the data. Relationships between recovery and geographical factors such as elevation, watershed area, and bedrock geology were not observed. There are differences in analyte concentrations associated with some of these variables, but these differences did not translate into different rates of change over time. The weak relationship between stream recovery and elevation, watershed area, and bedrock geology suggest most of the variation in the changes in the stream chemistry data is explained by time or an unknown and untested variable. Due to the evidence in the literature showing correlation between these geospatial variables and stream chemistry, this result is surprising (Cosby et al. 1991; Lovett et al. 1999; Weathers et al. 2000).

Based on the statistical analyses for bedrock geology, there were significant differences in SO_4^{2-} or ANC values among different bedrock classes, but no detectable differences in rates of recovery among bedrock classes. I can conclude, therefore, that streams in the mountains of Virginia are recovering from acidification at a relatively constant rate across bedrock lithologies. Sites underlain by basaltic bedrock had the highest ANC values while sites underlain by siliciclastic bedrock had the lowest ANC values on average. Additionally, sites underlain by siliciclastic bedrock had the highest sulfate values and sites underlain by granitic bedrock had the lowest sulfate values on average. These findings are consistent with those of other studies in the Shenandoah National Park area (Lynch and Dise 1985; Galloway et al. 1999; Cosby et al. 2006). These results further indicate that

previously identified relationships between bedrock geology and stream chemistry are not limited to the Shenandoah National Park area but extend more broadly throughout the mountains of Virginia.

While watershed area showed no relationship with indicators of stream acidity in our study area, elevation was loosely correlated with the change in SO_4^{2-} from 1987 to 2010 but not with ANC. In addition, the relationship demonstrated that as elevation increased, the change in SO_4^{2-} approached zero. Higher elevation sites were expected to exhibit a greater recovery from the years of acidification, and this would have been expected to manifest itself as a greater increase in ANC and decrease in SO_4^{2-} concentrations at the higher elevations. In fact, the data did not indicate a positive relationship between SO_4^{2-} concentration and elevation. This result is unexpected because higher elevation sites have been shown to be more influenced by acidic atmospheric deposition, and therefore were also expected to more dramatically show signs of recovery from atmospheric deposition (Lovett et al. 1999; Weathers et al. 2000). However, Robinson et al (2008) found greater time trends at low elevations for sulfate than at high elevations, and a mixed relationship between ANC and elevation, findings more consistent with our results. It is also possible that using site elevation rather than the maximum or mean elevation in the watershed have obscured true trends in chemistry based on elevation. It is also possible that what appears to be a relationship between elevation and SO_4^{2-} is really a geographic relationship (e.g., there are more high elevation sites in the southern part of the study area).

The observed differences between sites exposed to the gypsy moth and sites that avoided the gypsy moth defoliation are not consistent with expectations. The gypsy moth defoliation largely occurred in the 1990s and affected sites in the northern part of the study area. Therefore, effects of the gypsy moth defoliation such as decreased stream levels of SO_4^{2-} and ANC due to elevated NO_3^- would be expected to manifest in the 2000 sample season data. The sites with gypsy moth defoliation exhibit a decreasing trend with respect to time for sulfate, the same trend observed in the overall dataset and what we would predict given the decrease in deposition over time (Figure 8A). Conversely, the sites without the moth do not show as noticeable a downward trend, and in fact the 2000 sulfate values are slightly higher than the other two years. Similarly, the ANC results show almost identical means for the sites with and without defoliation for the 2000 and 2010 datasets, but slightly lower ANC values in 1987 for the sites that would eventually be affected by the moth (Figure 8B). While a decline in sulfate due to the gypsy moth defoliation would be consistent with the findings of Webb et al (1995), the corresponding increase in ANC is inconsistent with their findings and further supports the idea that the gypsy moth is not substantially affecting our results and that there is another driver to this spatial pattern other than the gypsy moth defoliation.

The differences in the patterns of SO_4^{2-} and ANC over time seen in the gypsy moth affected (northern) and unaffected (southern) sites are consistent with the map interpolation of the slope of stream SO_4^{2-} and ANC through the 3 study years (Figure 14). There is no clear pattern in slope of ANC, but sulfate appears to decline more substantially in the northern sites than the southern sites. Because these

differences were not found to be related to elevation, watershed area, or bedrock geology, the cause of the differences in slope of sulfur is likely due to an untested variable.

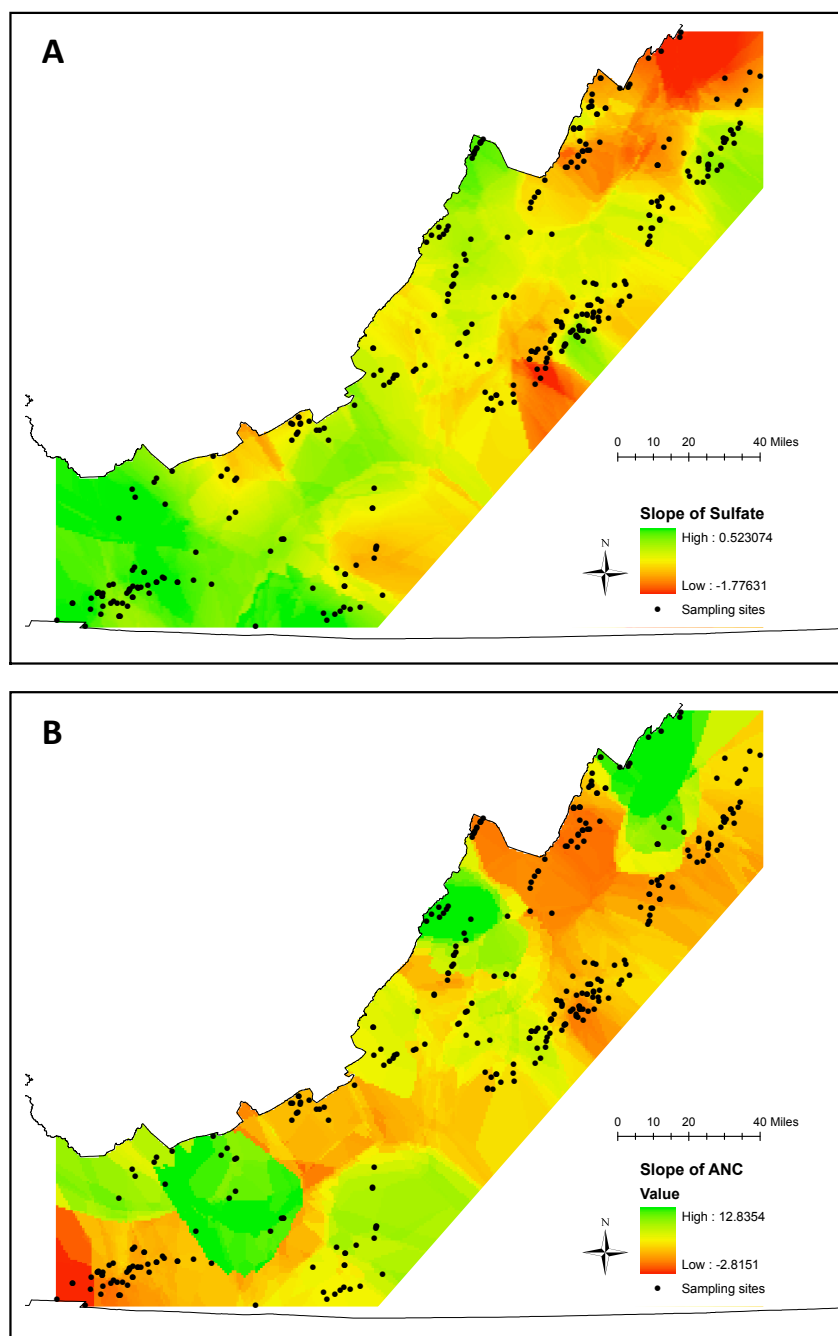
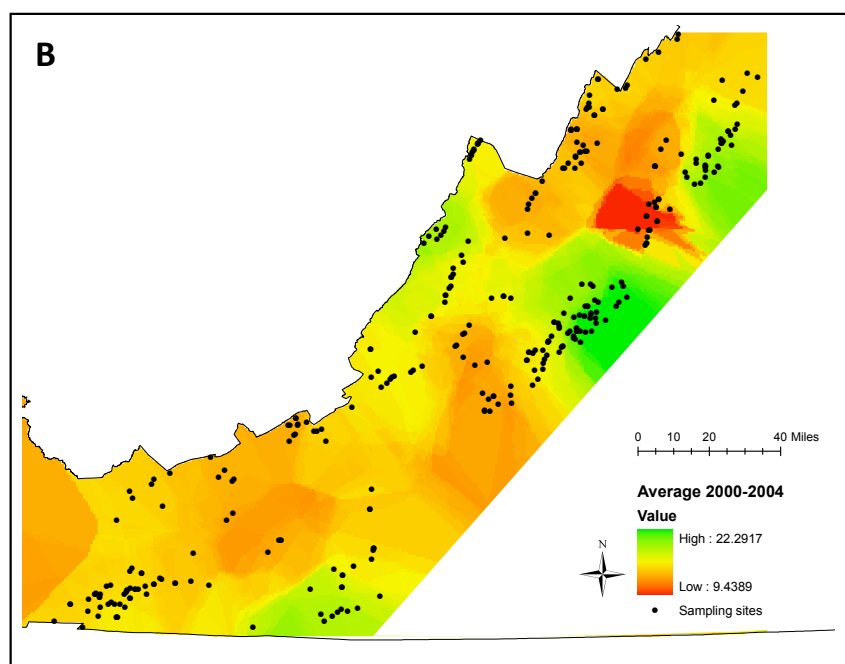
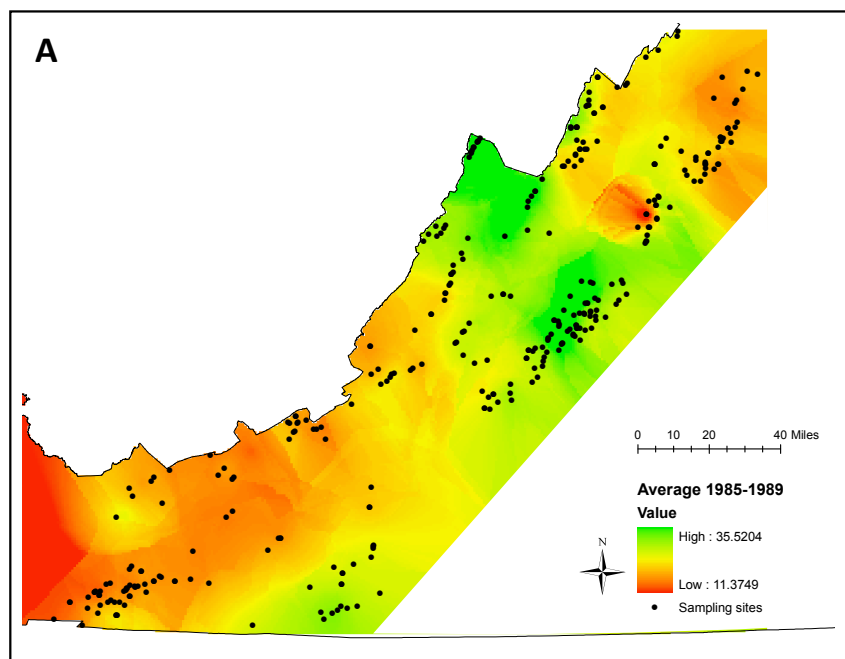


Figure 14. Slopes ($\mu\text{eq/L/year}$) of stream sulfate (A) and stream ANC (B) calculated for the 345 sample sites through the three study years. Map interpolation created using Esri Arcmap 9.3.1.

Mean atmospheric wet sulfur deposition has declined 60% from 1987 to 2009 across the VTSSS survey sites as calculated by a model used by the Clean Air Markets Division of EPA (Grimm and Lynch 2004). However, neither sulfur wet deposition nor the change in deposition over time are constant across the study area. Atmospheric wet deposition of sulfur is highest in the north central part of the study area and lowest in the southern corner (Figure 15A and B). These areas of high deposition are also experiencing the greatest reduction in sulfate wet deposition per year (Figure 15C) and correspond to the same general area that had the greatest rate of reduction in stream sulfate over the study period (Figure 14A). Therefore it is possible that the north-central region of the study area preferentially receives more deposition than other parts of the study region due to weather patterns and as sulfur emissions are reduced, these hotspot regions also experience the greatest declines in sulfate deposition and stream sulfate concentration. However, analysis testing the relationship of the slope of SO_4^{2-} wet deposition and the slope of stream SO_4^{2-} did not find a statistically significant relationship ($R^2=0.007$, $p=0.12$). In conclusion, while there appears to be spatial patterns in stream chemistry, the primary drivers of that pattern were not identified.



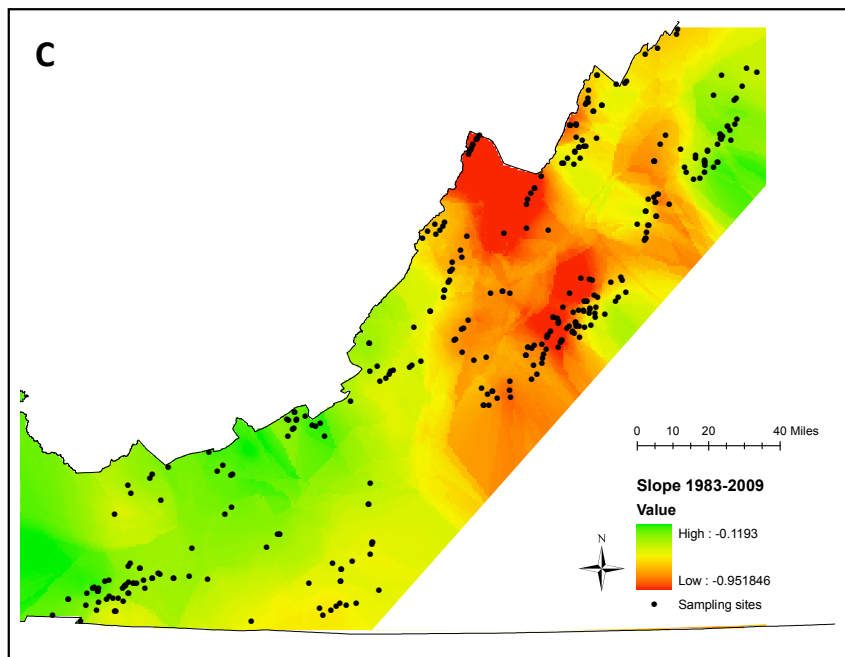


Figure 15. Map interpolation of wet deposition of sulfate (kg/ha/year) for the study area: annual average from 1985-1989 (A), annual average from 2000-2004 (B), and slope of deposition from 1983-2009. Data courtesy of the CAMD division of EPA.

5.5. Limitations of Analysis

Because this dataset was based on only three points in time, conducting true trend analysis was not possible. The use of environmental data provides limitations as well because the variables were not created by experimental design and external factors such as climate cannot be controlled. Many of the variables are spatially autocorrelated and, therefore, not truly independent. For instance, bedrock geology and elevation are non-randomly distributed throughout the watershed making it hard to distinguish those factors from each other or other spatial variables. The sulfur wet deposition data were calculated using an interpolation model based on only a few locations in the study area. The climate analysis would have been

improved by using site-specific runoff or discharge, but in the absence of those data we used Cl⁻ as a proxy. Detection of a possible gypsy moth effect could have been improved by use of a quantitative variable that provided estimates of the extent defoliation for each site's watershed rather than using a present/absent variable. Lastly, inferences made using the quarterly data can only provide limited information about the 345 survey sites. While the quarterly sites are a subset of the survey sites, they were chosen based on bedrock lithology and historic ANC values and are therefore not a true random sample of the parent population. Nonetheless, we are confident that the analysis supports the hypothesis that stream recovery from acidification is occurring due to emissions reductions of S and N.

5.6. Implications and future avenues of research

This project provides novel scientific insight into the duration of environmental effects from atmospheric deposition in the mountains of Virginia and will supply the EPA with information needed to make critical policy decisions. The proximity of the study sites to the high sulfur emitting utility companies provides added interest for evaluation of the efficacy of the CAAA. The findings of improved stream quality since the initial 1987 sampling period provide support to the benefits of the CAAA on aquatic systems. Despite the fact that atmospheric sulfate deposition is not expected to decline as much in the next 20 years as it has in the past 20 years, stream conditions in terms of acidity are expected to continue to improve and more streams should be suitable habitat for native brook trout. The increase in available brook trout habitat shows that improvements in water quality

through curbed emissions have had a detectable effect on populations of aquatic fauna.

The main causal factors for variation in stream response were not identified, and future analysis should further address this question. While a relationship between changes in wet deposition of sulfate and changes in stream sulfate was not found, a more thorough analysis of those variables may be the best place to begin future analyses given the spatial patterning in deposition observed.

While continuous monitoring of stream chemistry will be necessary to ensure the continuation of this trend in recovery, it would be useful to explore other, more contemporary questions this long-term monitoring program could answer. Climate change has become one of the more prominent and urgent dilemmas of recent years, and it would be worthwhile to adapt the VTSSS to monitoring the streams for evidence of climate change. Philip Stenger (unpublished analysis), director of University of Virginia's Climatology office, found that air temperatures are increasing significantly over the last 30 years in the southwestern mountain region of Virginia, but not the Central Mountain region. The differences in air temperature trends in different regions of the study area has unknown effects on stream chemistry. This, combined with the fact that temperature increases are likely to continue, provide good reason to look more closely at the affects of climate change on stream chemistry in the mountains of Virginia.

6. SUMMARY

This research established:

- Stream SO_4^{2-} concentrations have declined by 18% (12.9 $\mu\text{eq/L}$) and ANC concentrations have increased 76% (44.4 $\mu\text{eq/L}$) during the 23-year study period, a pattern consistent with stream recovery from acidification. While there was unexplained variance in the data, time was highly correlated with recovery from acidification.
- Bedrock geology was correlated with magnitude of concentrations of ANC and sulfate but was not related to rates of recovery from acidification.
- Stream elevation exhibited a weak but significant association with rate of recovery from acidification, with lower elevation sites showing slightly faster recovery.
- There was no relationship between watershed area and stream recovery from acidification.
- The gypsy moth defoliation of the 1990s did not appear to affect recovery from acidification.
- Spatial patterns in stream SO_4^{2-} and ANC were detected but were not related to the variables tested. Instead, variability in atmospheric sulfate deposition, which preferentially affects the north-central part of the study area may be an important factor in the spatial distribution of recovery.

The 2010 survey year was the lowest year on record for SO_4^{2-} and the highest year on record for ANC. While this recovery from acidification can largely be linked to the 60% decline in sulfate wet deposition over the course of the study period due to the CAAA, the delay in recovery suggests a role of additional factors in stream recovery besides the removal of the external source. While streams in the northern Appalachian region of the country showed substantial signs of recovery in the decade immediately proceeding the enactment of the CAAA, our sites in the mountains of Virginia have a more lagged response, a pattern attributed to greater sulfate adsorption by the soils. The substantial improvement of stream water quality in the 2010 dataset suggests that 2010 may be the year that sulfur inputs from the soils have declined enough to allow the streams in mountains of Virginia to show substantial signs of recovery. Future surveys will be able to address whether 2010 was truly a turning point for these streams or if they appeared less acidic for other reasons.

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