Acidification in upland watersheds of western Virginia: biogeochemical responses to reduced acid deposition and predictions for future interactions with climate change

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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
April, 2014

Abstract

Although decreased acid deposition over recent decades has led to widespread recovery of surface waters across the U.S. and Europe, high sulfate (SO_4^{2-}) adsorption in the southern Appalachian uplands has prevented significant acid-base recovery in this region. To update the regional acid-base status and characterize the controls on watershed response to reduced acid deposition, streamwater samples collected at 64 sites in western Virginia on a quarterly basis from 1987 to 2011 were analyzed for chemical properties. Individual watershed response was strongly influenced by the dominant underlying bedrock, which affected SO_4^{2-} adsorption and base cation supply. Although pH increased at a majority of sites across all bedrock types, acid neutralizing capacity decreased at most sites underlain by base-poor bedrock, suggesting the susceptibility to episodic acidification remains a serious threat to these streams. Results of a sulfur mass balance analysis indicate that sustained declines in sulfur deposition may lead to general decreases in the pool of stored sulfur in base-poor siliciclastic watersheds, which until recently have been experiencing net storage of sulfur.

At the same time, as anthropogenic climate change continues to emerge as a global phenomenon affecting temperature regimes and hydrological cycling among many other variables, new concerns are being posed to these watershed ecosystems. The PnET-BGC model was applied to the White Oak Run (WOR1) watershed in Shenandoah National Park, VA to evaluate the potential influence of future changes in climate on acid-base chemistry. While the streamwater concentration of SO_4^{2-} is projected to decline as WOR1 recovers from peak deposition in the 1970's, base cations are expected to decline even more in part as a result of increased plant demand, leading to an overall loss of alkalinity in the stream. The chemical forecast for WOR1 is dependent on the exact magnitude of change in climate, with precipitation

and temperature having interactive effect on several relevant watershed processes, including drainage, mineralization, and vegetative demand. These projected impacts of climate change will likely diminish some of the gains in stream alkalinity as a result of the Clean Air Act and subsequent amendments.

The results of this project are valuable not only in deepening the understanding of these biogeochemical cycles independently and interactively, but also in assessing and informing policy with regard to the projected impacts of climate change and acid deposition on these sensitive aquatic systems. There is significant opportunity to continue and enhance the research presented here, including expanding the analyses to new watersheds and investigating trends on smaller timescales.

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Acknowledgements

The research that is presented here is in no way an individual effort, and I owe an incredible amount of thanks to the numerous individuals who have helped in all facets of my work and graduate career. Foremost, I would like to thank my advisor, Dr. Todd Scanlon, for his time and guidance throughout the project and for fostering my research abilities. I would also like to thank my committee members, Dr. Jack Cosby, Dr. James Galloway, and Dr. Michael Pace for their feedback and support.

Work put in by the other current and former members of the Shenandoah Watershed Study program provided the foundation upon which this entire project was built. Specifically, the efforts of Rick Webb and Susie Maben to the entire SWAS program and to my work specifically are nearly impossible to fully appreciate. Thanks to Jeff Atkins for doing all the dirty work and letting me join in sometimes. Furthermore, I must thank Karen Rice for her enthusiasm and encouragement.

I would be remiss if I did not thank the entire Environmental Sciences Department, students, faculty, and staff, for providing an incredibly supportive atmosphere in which to work. I specifically thank the Brick House for making our house a home and keeping it clean; Annie Dunckel for being the best GSA colleague I could ask for; Cindy Allen for helping me with every departmental question imaginable and doing it with a smile; and to Susie and John Maben for keeping me company on the ground floor. Finally, I would like to thank my family for listening and always being there.

Chapter 1: Introduction

1. Acid deposition in western Virginia

Acid deposition has been a major global biogeochemical driver for decades, adversely affecting landscapes across the U.S. and Europe (Stoddard et al., 1999; Kahl et al., 2004; Driscoll et al., 2007). Acid deposition occurs when sulfur dioxide (SO_2) and nitrogen oxides (NO_x) are emitted to the atmosphere, oxidized, and eventually deposited across the landscape. At certain levels, these acidic compounds can have many negative effects on human health and the environment, including the degradation of air quality, impairment of visibility, damage to sensitive forests and coastal ecosystems, and acidification of lakes and streams (Burns et al., 2011).

Acid deposition in the Valley and Ridge and Blue Ridge (Ridge/Blue Ridge) physiographic provinces of western Virginia is dominated by sulfur (Sullivan et al., 2003, 2004). Total deposition of sulfur has been two to four times greater than inorganic nitrogen species over the entire period of observation (1982-present) (NADP, 2012), and in general, nitrogen has not been a major factor in the acid-base status of Ridge/Blue Ridge streams (Webb et al., 2004). As such, discussions of long-term acidification of streams in western Virginia focus predominantly on sulfur rather than nitrogen.

Since the passage of the Clean Air Act in 1970 and the subsequent amendments in 1990, SO_2 emissions and acid deposition have declined significantly across the U.S., including the Ridge/Blue Ridge regions (Chestnut and Mills 2005). Many acid sensitive regions in the northeastern and midwestern U.S. have responded positively, showing recovery or stabilization in acid-base status over the past three decades (Skjelkvåle et al., 2005). Unfortunately, base-poor watersheds in the Ridge/Blue Ridge regions have experienced little to no recovery despite the significant decrease in sulfur deposition (Webb et al., 2004; Skjelkvåle et al., 2005). Previous studies have attributed this difference to a higher relative sulfate (SO_4^{2-}) adsorption capacity of watershed soils in the region (Webb et al., 1989; Turner et al., 1990; Webb et al., 2004) and to limited base cation supplies (Bricker 1986; Herlihy et al., 1993; Hyer et al., 1995; Webb et al., 2004).

The high sulfur retention of soils in the Ridge/Blue Ridge contributes to a significant lag time in surface waters responding to reduced sulfur deposition, indicating the effects of acid deposition will likely continue for decades (Manderscheid et al., 2000). Thus, continued monitoring remains critical in assessing the responses of watersheds in this region to further changes in acid deposition and gauging the prospect of recovery.

2. Interaction of climate with watershed acidification

As anthropogenic climate change continues to develop as a global phenomenon affecting temperature regimes and hydrological cycling among many other variables, new concerns are being posed to these watershed ecosystems. This includes affecting many biogeochemical processes, including watershed acidification and recovery.

The Earth has warmed by an average of 0.74°C between 1906 and 2005 (IPCC, 2007), with the southeast U.S. warming 1.9°C between 1901 and 2008 (Karl et al., 2009). The effects of climate change on streams in western Virginia are already evident. A basic trend analysis of stream temperature measurements at four monitored sites in Shenandoah National Park, VA (SHEN) reveal that climate change may be impacting these systems already (Figure 1). All four systems have significantly increasing temperature trends over their respective records (20-33 years). These trends correlate well with the overall climate pattern during the same time span, where annual mean temperature increased at a rate of 0.03°C yr^{-1} from 1980 to 2012. Discharge has also varied over time, though insignificantly in any single direction, thus not affecting a general trend in stream temperature to any substantial degree.

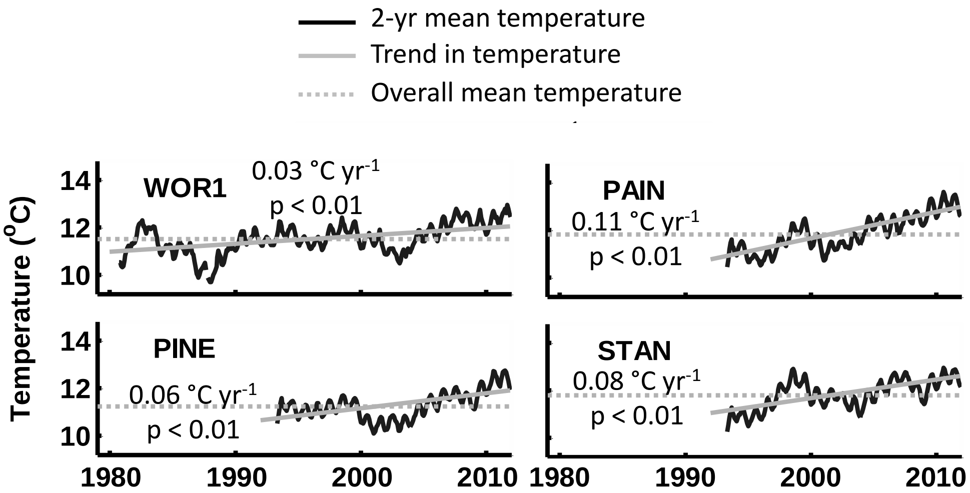

Figure 1: Trends in the temperature of four streams in Shenandoah National Park, VA measured weekly. The streams are White Oak Run (WOR1), Paine Run (PAIN), Piney River (PINE), and Staunton River (STAN).The overall and two-year mean temperatures are shown to give perspective of variation over longer time periods. Trends were calculated for the entirety of record using the Seasonal Kendall Tau test.

Issues associated with climate change are numerous and diverse, but two key elements stand out: the expected increase in temperature and a potential change in water availability. The ongoing and future changes associated with these variables are likely to vary across the globe, but universally they have substantial implications for biogeochemical cycling, including the response of ecosystems to acid deposition (Boisvenue and Running, 2006). For example, temperature increases generally speed up: plant growth (Rustad et al., 2000), decomposition (Kirschbaum 1995), and nutrient cycling (White et al., 1999; Dalias et al., 2002). In terms of precipitation, changes in hydrologic cycling have serious implications for the severity of episodic acidification (Wigington et al., 1990), forest productivity (Boisvenue and Running, 2006), soil respiration (Davidson et al., 2000), and fire frequency (Flannigan et al., 2000).

These potential changes in temperature regimes and hydrological cycling as a result of climate change are extensive, likely leading to diverse ecological and biogeochemical impacts in coming decades. The work presented here investigates the past, present, and future state of acidification in watersheds of western VA, which includes accounting for potential effects and interactions of acid deposition and climate change in the future.

3. Thesis Organization

This thesis is organized as two self-contained papers, both related to the biogeochemistry of watershed acidification in the mountainous region of western Virginia. Chapter 2 examines the current trends in acidification and recovery in 64 streams in the region and the biogeochemical controls on those changes. A detailed analysis of these systems was last published in 2004 (Webb et al., 2004) and the geochemical controls on individual watershed response to changes in deposition are not well characterized. The manuscript presented here successfully accomplishes the former task and provides significant development on the latter. It also reports that depletion of the stored pool of sulfur might be occurring at a base-poor watershed for the first time in its 34-year record, signifying an important precursor for further improvements in acid-base status.

In Chapter 3, the potential influence of future climate change on acidification and recovery at a single watershed in SHEN is explored. The potential effects of climate change on watershed biogeochemical processes are widespread and diverse, thus the consideration of climate change is necessary in projecting future trends in acid-base chemistry. This study is the first modelling application to an upland watershed in the region to consider potential changes in climate and its effect on vegetation, nutrient cycling, and acid-base chemistry.

A summary of the entirety of this work and likely implications from the results are presented in Chapter 4. Potential avenues of future research, to improve and expand upon the findings of this thesis, are also included. Continued monitoring and research on watershed biogeochemistry with respect to acidification and recovery is necessitated by the ongoing deterioration of many watersheds in the region and the possibility for climate change to further acidify affect these systems.

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Chapter 2: Roles of sulfate adsorption and base cation supply in controlling the chemical response of streams of western Virginia to reduced acid deposition

Abstract

Decreased acid deposition over recent decades has led to reductions in streamwater acidity on a widespread basis throughout the U.S. and Europe. A notable exception has been the central Appalachian Mountains of the southeastern U.S., where declines in acid deposition have not translated into similar trends in stream chemistry in these watersheds with highly-weathered soils. To better characterize this observed behavior, streamwater samples collected at 64 sites in western Virginia on a quarterly basis from 1987 to 2011 were analyzed for chemical properties. Individual watershed response was strongly influenced by the dominant underlying bedrock, which affected sulfate (SO_4^{2-}) adsorption and base cation supply. Overall, pH increased at a majority of sites across all bedrock types. However, acid neutralizing capacity (ANC) decreased at most sites underlain by base-poor bedrock, suggesting the susceptibility to episodic acidification remains a serious threat to these streams. The declines in ANC were more closely related the depletion of base cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) rather than increased SO_4^{2-} concentration. Sites with higher relative SO_4^{2-} adsorption exhibited little change in ANC. A mass balance analysis of sulfur at a base-poor watershed revealed that exports have recently surpassed inputs for the first time within the several-decade period of record. This trend appears likely to continue, and if sustained, the depletion of the stored pool of sulfur signifies an important precursor for further improvements in streamwater acidity in the region.

1. Introduction

Reductions of sulfur dioxide and nitrogen oxide emissions as a result of the Clean Air Act implementation in 1970 and subsequent amendments in 1990 have led to significant declines in acidic deposition across the U.S. (Chestnut and Mills 2005). Long-term monitoring efforts have revealed that acid sensitive regions across the U.S. and Europe most affected by deposition have responded positively, showing improvement in acid-base status over the past three decades (Skjelkvåle et al. 2005). A notable exception to the pattern of response is the southeastern U.S., primarily the upland areas of the Valley and Ridge and Blue Ridge physiographic provinces (Ridge/Blue Ridge) of the central Appalachian Mountains. Previous studies in this region have reported little to no change in streamwater pH or acid neutralizing capacity (ANC). This is despite a significant decrease in the deposition of major acid anions over the past 30 years in the mid-Appalachian region, as represented by the trends in wet deposition in Shenandoah National Park (SHEN; Figure 1) (Webb et al. 2004a; NADP, 2012). With this ongoing trend in deposition and the emergence of other global biogeochemical factors such as climate change imposing new influences on these ecosystems, continued monitoring remains critical in assessing the acid-base status and outlook of watersheds in this region. Such efforts can elucidate the drivers aiding or impeding acidification and can assess whether the patterns conform to theoretical expectations and behavior observed at other sites where chemical responses have been more immediate. This paper aims to identify the specific biogeochemical factors controlling the response to reduced acid deposition in watersheds of the central Appalachian Mountains in western Virginia.

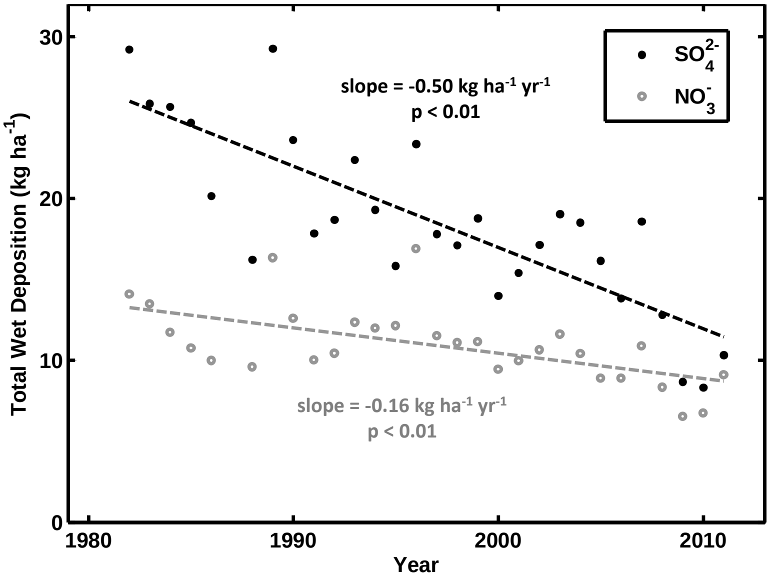

Figure 2: Time series showing the significant decrease in wet deposition of SO$_4^{2-}$ and NO$_3^-$ at Big Meadows (VA28) in Shenandoah National Park, VA (NADP 2012).

1.1 Acidification: Theory and Observations

The acid-base status of a stream is most often quantified in terms of pH and ANC, with the latter measuring of the ability of an unfiltered water sample to neutralize strong acids (Hemond 1990). While pH is a primary indicator of the chronic acid-base status of streamwater, ANC is more closely linked to episodic acidification. Low ANC has been related to reduced species richness and declining populations of both fish and aquatic invertebrates (Lien et al. 1996). By definition, surface waters with ANC values between 0 and 50 μeq L^{-1} are considered susceptible to episodic acidification (Wigington et al. 1993). These episodes are associated with significant decreases in pH, which may persist over a period of a few hours to several weeks. It has been shown that the elevated concentrations of dissolved monomeric aluminum during acidic episodes can lead to significant fish mortality over the course of a single event and is a critical factor in determining the viability of fish and aquatic invertebrate populations in streams (Baker et al. 1996; Bulger et al. 2000; Kowalik and Ormerod 2006). Thus, ANC is a critical indicator of ecological vulnerability to acidification.

In terms of changes in surface water acidity, the direction of change in ANC is determinant. Streams that are becoming more prone to episodic acidification exhibit a negative trend in ANC. Decreases in ANC can be caused by declines in the supply of base cations (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}) or by additions of acidic anions, like SO_4^{2-} or nitrate (NO_3^{-}) (Dentener 2006). In streams of the Ridge/Blue Ridge region, SO_4^{2-} is found in much greater concentrations than NO_3^{-} (Webb et al. 1995; Webb et al. 2004a). As such, the remaining analysis and discussion is focused primarily on acidification of surface waters by SO_4^{2-}.

The effect of acid deposition on surface waters depends not only on the intensity of deposition, but also on factors associated with soil storage. Adsorption of SO_4^{2-} by watershed soils is the most important process regulating SO_4^{2-} concentration in associated surface waters (Chao et al. 1962; Singh 1984). All other conditions being equal, weathered soils have a higher SO_4^{2-} adsorption capacity (SAC) than younger soils due to the accumulation of iron and aluminum oxide and hydroxide minerals in the more mature soils (Sokolova and Alekseeva 2008). In the U.S., soils with high SAC are commonly found in regions unaffected by the most recent glaciation, the Late Wisconsin Glaciation, such as in the southeastern U.S. (Reuss and Johnson 1986; Rochelle et al. 1987). Soils with lower SAC, like those found in the northeast U.S., respond more quickly to changes in atmospheric deposition because of their lower levels of retention (Cosby et al. 1986). Accordingly, decreases in surface water SO_4^{2-} concentrations have been observed in these regions (Skjelkvåle et al. 2005).

Another key attribute controlling surface water response to acidification is the supply of base cations (Stoddard et al. 1998). Mineral weathering acts as the primary source of base cations to catchments, with atmospheric deposition typically contributing minimally to the total base cation budget (Currie et al. 1996). Watersheds with a greater supply of base cations will more effectively buffer acidic input compared to a system with a lower content (Houle 2006). However, long-term exposure to acidic deposition depletes base cations from soils, limiting the export to surface waters (Fernandez et al. 2003).

1.2 The Valley and Ridge and Blue Ridge Physiographic Provinces as a Distinct Region

Geology acts as a major distinguishing factor for watersheds of the Ridge/Blue Ridge provinces from areas in the U.S. where significant changes in acid-base status have been observed. For example, the elevated SAC, which resulted from being exempted from the most recent glaciation, has decreased the potential for rapid acidification of surface waters in the region (Turner et al. 1990; Webb 2004b). However, the retention of SO_4^{2-} is limited to a finite capacity, and upon exceedance, SO_4^{2-} export can increase causing further surface water acidification. The high SAC of Ridge/Blue Ridge catchments has also contributed to the lack of response to reduced sulfur deposition.

Base cation concentrations are also greatly influenced by geology in this region. The base cation supply to a watershed is highly dependent on the underlying bedrock (Webb et al. 2004a). For the bedrock classes present in the Ridge/Blue Ridge region that underlie upland watersheds, mafic has a much greater weathering potential than felsic or siliciclastic bedrock (Grieve 1999). These potentials result from differences in the stability of constituent minerals and base cation content. The supply of base cations to watersheds in this region is further limited by depletion as a result of the accelerated leaching from soils caused by the long history of acid deposition and uptake by vegetation, especially in watersheds where forests are undergoing aggradation.

Together, SAC and base cation supply have shaped the trajectory of acidification in the Ridge/Blue Ridge region and have contributed to the observed declines in both pH and ANC of streams as reported in previous analyses (Webb et al. 2004a; Skjelkvåle et al. 2005). Analysis of stream chemistry must therefore include considerations of watershed soils. This is most obvious in the case of SO_4^{2-}, where soil SAC significantly limits the amount^{-} reaching streams. Furthermore, with the large pool of stored SO_4^{2-} in the soils, the effects of acidic deposition will be observed for decades to come (Sullivan et al. 2008), as some amount of the stored SO_4^{2-} gradually desorbs and is exported via stream flow.

Increases in the ANC of acidified waters are restricted not only by acid anion export, but also by base cation export. Unfortunately, the already depleted watersheds and the base-poor bedrock impose a limitation on improvement as the potential for resupply of base cations is low and limited by kinetics. This combination of characteristics in the Ridge/Blue Ridge region is quite different from that of the northeastern U.S., where most research examining the consequences of reduced acid deposition has been conducted. Although it has been known for some time that Ridge/Blue Ridge systems behave differently, the mechanisms by which they have responded to decades of decreased acid deposition remain insufficiently characterized.

1.3 Objectives

The objectives of this paper are to (1) provide a summary of the status of acidification in streams within the Ridge/Blue Ridge region of Virginia, (2) characterize the geochemical components associated with any long-term trends, and (3) investigate potential factors that have driven these trends. We address these objectives through trend analysis applied to quarterly data from 64 streams within the Ridge/Blue Ridge region of Virginia, spanning a period from 1987-2011 and in the context of a more detailed weekly time series collected at White Oak Run

(WOR1) from 1979-2011. We report that while pH has increased at a majority of sites across all bedrock types, observed declines in ANC at most sites underlain by base-poor bedrock suggests episodic acidification remains a serious threat to these streams. Biogeochemical processes that have influenced these trends are investigated and the findings are placed in context of previously observed patterns from sites in the northeastern U.S. and northern Europe. This study also has implications for researchers and policymakers in assessing the continued effectiveness of the Clean Air Act and associated amendments.

2. Methods

Stream chemistry data were collected as part of the Shenandoah Watershed Study (SWAS) and the Virginia Trout Stream Sensitivity Study (VTSSS; swas.evsc.virginia.edu). Our analysis focuses on data from 64 streams sampled quarterly since 1987, selected because of their continuity of record and lack of landscape disturbance or manipulation within the surrounding watershed. For a more detailed analysis of watershed sulfur dynamics, we also examined weekly data from White Oak Run (WOR1), a base-poor watershed underlain by siliciclastic bedrock in Shenandoah National Park, VA. Weekly stream chemistry data and daily discharge estimates have been collected at this site since 1979.

2.1 Site Description

All watersheds included this study are located in upland portions of the Valley and Ridge or Blue Ridge physiographic provinces of western Virginia (Figure 2) (Fenneman 1928). Watersheds are typically small to intermediate in size (< 20 km^2) with main channels typically 5 – 10 km in length. Although the area’s land use history includes agriculture, timber harvesting, and human habitation, most of this activity ceased 50 – 100 years ago (Webb et al. 1989; Cosby et al. 1991). Land cover is dominated by deciduous forest (Virginia Dept. of Forestry 2005).

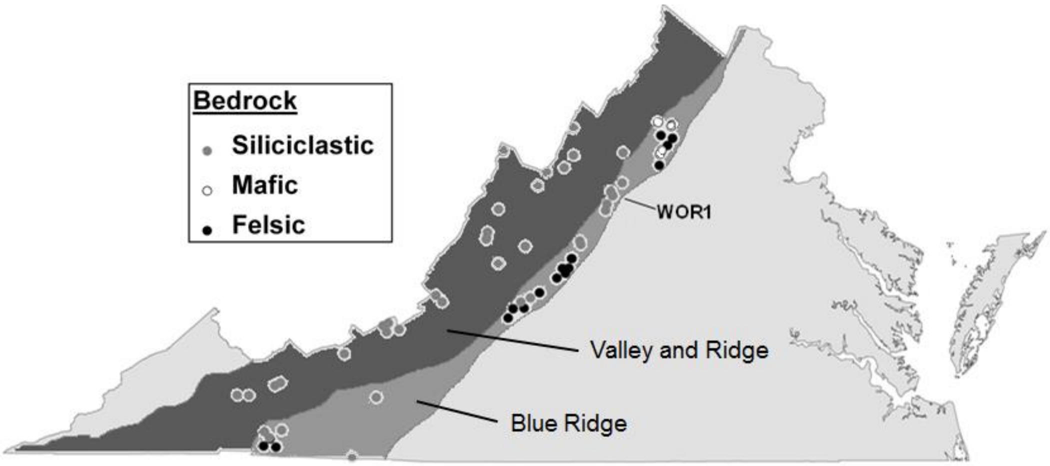

Figure 3: Map of 64 studied watersheds, classified by bedrock, distributed across the Valley and Ridge and Blue Ridge physiographic provinces of Virginia. WOR1 is labeled because of the additional analyses performed using data from this site.

The main bedrock types in this region include crystalline rocks (felsic and mafic) along the crest and eastern flank of the Blue Ridge province, with sedimentary rocks (siliciclastic) along the western flank of the Blue Ridge province and on the ridges of the Valley and Ridge province. All three classes of bedrock are represented in this study. Of the 64 streams sampled on a quarterly basis, 43 sites are underlain primarily (> 50%) by siliciclastic, 5 by mafic, and 16 by felsic. It is important to note that this distribution of bedrock classes is not representative of all the watersheds in western Virginia, as the original site selection intentionally targeted watersheds that were more susceptible to acidification (i.e. siliciclastic).

2.2 Sample Collection and Analysis

All water samples analyzed in the quarterly and weekly datasets were collected by grab sampling. Samples were preserved using 0.5 mL of chloroform per 500 mL of sample and stored at room temperature. Included in this study are measurements of ANC, pH, SO_4^{2-}, and base cations. The sum of base cations (SBC) was calculated by summing all individual cation concentrations.

Prior to October 2006, water samples were measured manually for ANC (APHA 1985) and pH (APHA 1998) using a standard pH meter and electrode. Beginning in October of 2006, an automated titration system was utilized in measuring pH and ANC (U.S. EPA 1987; Gran 1952). Prior to October of 2005, cations were measured using an atomic absorption spectrophotometer using EPA based methods for each cation (U.S. EPA NERL 1971). Sulfate was analyzed using ion chromatography methods based on EPA Method 300.1 (U.S. EPA 1997). Beginning in October of 2005, an ion chromatography system was used to analyze both SO_4^{2-} (EPA Method 300.1; U.S. EPA 1997) and cations (ASTM Method D 6919-03; ASTM 2003).

The upgrade and replacement of instrumentation in 2005-2006 created statistically significant, albeit small, changes in all analyte measurements except Mg^{2+} as determined by a paired t-test. To adjust for this, a linear correction was applied to all measurements made by the old instrumentation to align values to the newer instrumentation. For ANC and pH, 95 samples were used in this linear correction. For ions, nine samples were measured by each method a total of four times, and the average values were used for correction (N = 9). Correlation in all method comparisons was high ($r > 0.95$), providing confidence in the accuracy of these adjustments. The significance of the instrumental change as determined by a paired t-test and the correction scalar and constant are all shown in Table 1 for each analyte. The relationships used for corrections are assumed to be constant for the entire timeframe of analysis. Adjusted data were used in all analyses.

Table 1: Significance associated with the methods change and subsequent correction factors to align data collected using old instrumentation to the newer instrumentation. Median values from the sets of compared data are shown to give perspective to relative concentrations or levels of each analyte. Data collected using older instrumentation was adjusted using the corresponding coefficient and intercept.

	Median			Correction Factors	
Analyte	Old Method	New Method	*p-value of t-test*	Coefficient	Intercept
ANC (μeq L^{-1})	34.04	43.15	< 0.01	1.01	6.64
pH	6.45	6.32	< 0.01	0.96	0.16
SO_4^{2-} (μeq L^{-1})	55.54	53.92	0.01	1.03	-2.45
Ca^{2+} (μeq L^{-1})	92.57	96.95	0.03	1.06	-1.79
Mg^{2+} (μeq L^{-1})	90.83	93.33	0.06	-	-
K^+ (μeq L^{-1})	12.01	11.41	< 0.01	1.03	-1.04
Na^+ (μeq L^{-1})	28.83	28.77	< 0.01	1.00	-0.39

2.3 Statistical Analysis

Trend analysis was conducted for every measured variable, including SBC, at each site using the Seasonal Kendall Tau test (SKTT; Hirsch et al. 1982). The SKTT is the most commonly used method for detecting site-specific trends in water quality data because it accounts for non-normal distributions, seasonality, and missing values. Moreover, the modified SKTT can also accommodate serial correlation (Hirsch and Slack 1984). Sen's method was used to determine a single trend value for each constituent at each site (Sen 1968). To determine whether each bedrock class tended toward positive or negative trends, the Wilcoxon Signed Rank test was employed. A significance criterion of 0.05 was utilized in all significance testing.

A mass balance analysis of sulfur was performed at WOR1. Total wet sulfur deposition data obtained from the National Atmospheric Deposition Program/National Trends Network for Big Meadows (VA28) in SHEN was used for WOR1 because of the close proximity (40.8 km) of the two sites (NADP 2012). The ratio of wet to dry sulfur deposition at WOR1 from the Community Multiscale Air Quality (CMAQ) model, 0.910, was employed to estimate total sulfur deposition for each year of record (Byun and Ching 1999). Stream export of sulfur was calculated using LOADEST (Runkel 2004), while utilizing all weekly measurements of SO_4^{2-} in the period of record and daily discharge estimates. Total sulfur storage was calculated for each year of record at each watershed and is reported in kg S ha^{-1}.

3. Results

Over the timeframe of study (1987-2011), 63% of all monitored streams demonstrated a negative trend in ANC, indicative of decline in this measure of acid-base status (Figure 3a). Meanwhile, in terms of pH, 64% of streams displayed a positive trend (Figure 3b), with each bedrock class displaying a significantly positive median trend of +0.010 pH units yr^{-1} or less. The distribution of trends in ANC is clearly influenced by the dominant bedrock of a particular watershed. Acidification, classified by a negative trend in ANC, was associated primarily with the base-poor siliciclastic sites (median = -0.19 µeq L^{-1} yr^{-1}). All mafic sites exhibited a positive trend in ANC (median = +1.14 µeq L^{-1} yr^{-1}), while felsic sites were split, with nine sites increasing and seven sites decreasing. Trends in SBC were mainly negative, although only the siliciclastic group (median = -0.23 µeq L^{-1} yr^{-1}) was significantly so in this direction (Figure 3c). Individual base cations are not discussed because of differences in the distribution of each ion in the three bedrock classes. The mafic and siliciclastic bedrock groups exhibited declines in SO_4^{2-} concentration (Figure 3d), with significantly negative median values of -0.32 µeq L^{-1} yr^{-1} and -0.09 µeq L^{-1} yr^{-1} respectively.

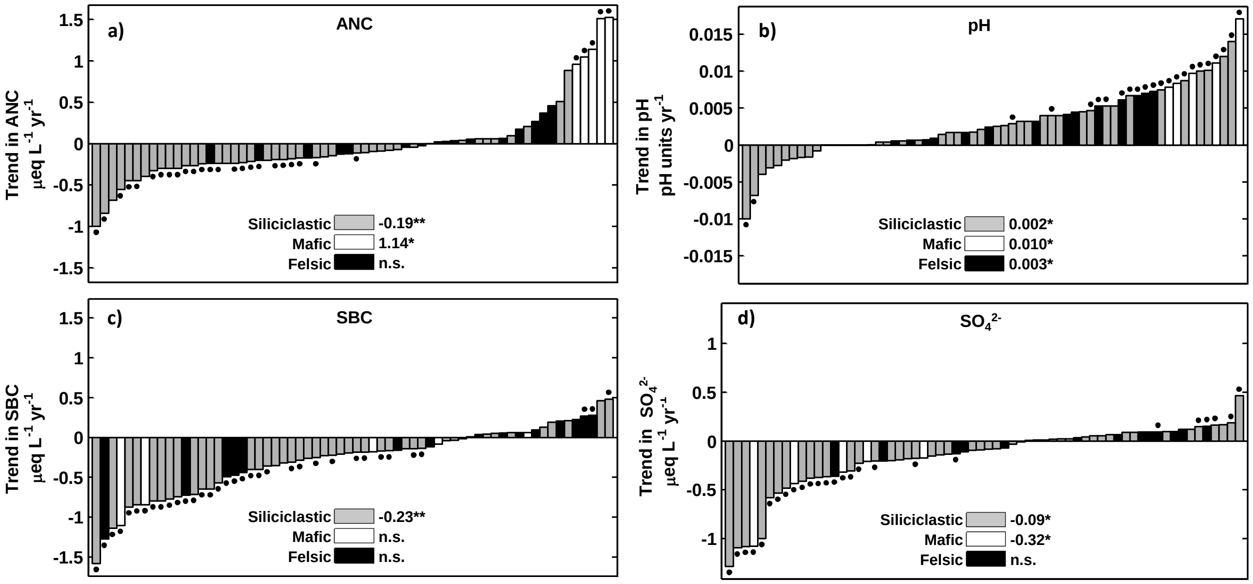

Figure 3: Bar charts displaying ranked trends of all 64 quarterly sampled sites for (a) ANC, (b) pH, (c) SBC, and (d) SO_4^{2-} (1987-2011). Significance of an individual trend at a 95% confidence level is indicated by a dot (·). Median trends for each bedrock class are shown for each analyte if the median is biased positive or negative. * Represents significant bedrock trend at a 95% confidence level, and ** significant at a 99% confidence level.

For further analysis, watersheds were separated into two groups based on whether the trend in ANC was positive or negative, regardless of bedrock classification. The trends in ANC of these two groups were regressed versus the trends in SO_4^{2-} and SBC, the two main controls of ANC for this region. This analysis was performed in order to ascertain if these two variables affected sites with increasing and those with decreasing ANC in notably different manners (Figure 4). Of those watersheds with increasing ANC (Figures 4a and b), trends in SO_4^{2-} explain nearly half of the variance ($r^2 = 0.45$, $p < 0.01$) in the trends in ANC, while trends in SBC are poorly related ($r^2 = 0.10$, $p = 0.36$). Of those watersheds with decreasing ANC (Figures 4c and d), trends in SBC concentration best explain ($r^2 = 0.51$, $p < 0.01$) the trends in ANC. Trends in SO_4^{2-} ($r^2 = 0.02$, $p = 0.24$) do not relate well with the trends in ANC at these sites.

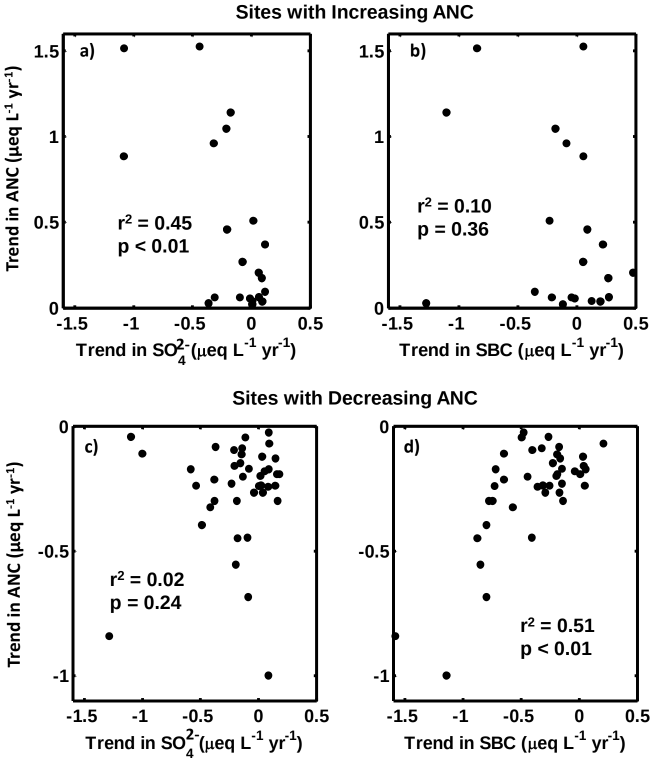

Figure 4: Linear regression of the trends in ANC versus the trends in SO_4^{2-} and SBC separated for sites that show increasing ANC (a and b) over the time period and sites that show decreasing ANC (c and d).

The average initial concentration of SBC, defined as the average concentration over the first two years of monitoring, positively relates with the trend in ANC (Figure 5a, $r^2 = 0.35$, $p < 0.01$). The average initial concentration of SBC is used here as a measure of the base cation supply to a watershed, with greater initial concentrations indicating a greater supply. Initial concentration is used rather than average the concentration over the entire period of observation to minimize changes in concentrations during the study, in particular depletion over time. Of note are the median initial SBC concentrations of the bedrock classes in relation to one another. Mafic watersheds display a much greater initial SBC concentration (median = 342 μeq L^{-1}) than either felsic (146 μeq L^{-1}) or siliciclastic (133 μeq L^{-1}) sites, demonstrating the greater base cation supply of watersheds underlain by mafic bedrock.

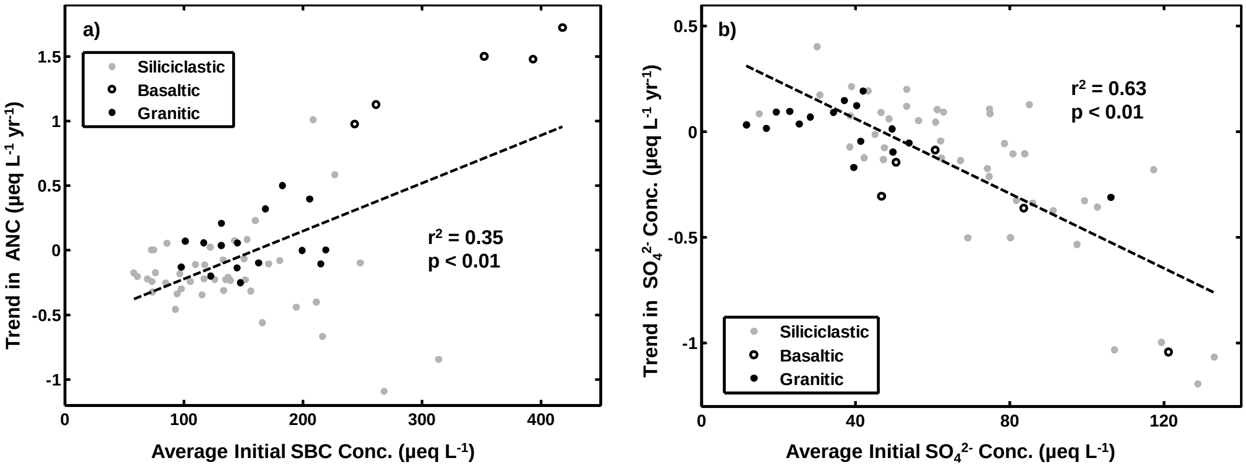

Figure 5: Regression of (a) the trends in ANC versus the average initial SBC concentration and (b) the trends in SO_4^{2-} versus the average initial SO_4^{2-} concentration for all 64 sites. Note the clear distinction between bedrock classes and the initial condition for both SBC (mafic markedly greater) and SO_4^{2-} (felsic markedly lower).

In a similar analysis, the trend in SO_4^{2-} is inversely related to the initial concentrations of SO_4^{2-} and explains over 63% of the variance (Figure 5b, $p < 0.01$). The concentration of SO_4^{2-} represents the relative SO_4^{2-} retention in individual watersheds. Since all sites are exposed to approximately equivalent deposition, lower surface water concentrations of SO_4^{2-} indicate higher retention in watershed soils. In this relationship, felsic watersheds are distinguished as having a greater SO_4^{2-} retention, with a median initial SO_4^{2-} concentration of 36.2 μeq L^{-1}, which is nearly half that of both mafic (57.1 μeq L^{-1}) and siliciclastic (63.5 μeq L^{-1}) sites.

4. Discussion

4.1 Patterns in ANC and pH

Overall, ANC has decreased in a majority of monitored watersheds in the Appalachian Mountains of Virginia over the last 25 years. This finding is consistent with those reported nearly a decade ago for most watershed studies in this region (Webb et al. 2004a; Skjelkvåle 2005). Retention of SO_4^{2-} in watershed soils and base-richness of the underlying bedrock appear to act as the main controls on individual watershed response. Sites underlain by base-poor siliciclastic bedrock have experienced the majority of the decline in ANC, base-rich mafic watersheds have seen improvements in stream ANC, and felsic watersheds have been relatively stable over the period of record owing to the higher SAC.

Although the trends in ANC indicate the overall acid-base status of the region's surface waters has deteriorated, the trends in pH suggest just the opposite, increasing at a clear majority of sites across all bedrock classes. One potential reason for this difference could be changes in organic matter quantity or quality over the period of record. Discrepancies in ANC and pH trends have previously been attributed to changes in organic acidity (Evans et al. 2001). Furthermore, variation in organic matter quantity (Montieth et al. 2007) and quality (Donahue et al. 1998; SanClements et al. 2012) have been noted in areas that have experienced changes in soil ionic strength driven by changes in atmospheric deposition. Despite having a difference in direction, the trends in ANC and pH are significantly correlated ($r^2 = 0.38$, $p < 0.01$; Figure 6).

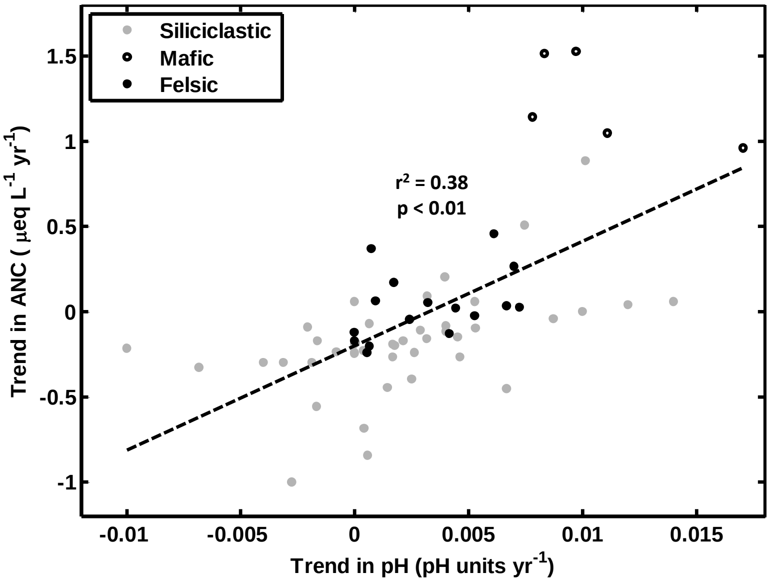

Figure 6: Regression of the trends in ANC versus the trends in pH for all 64 sites. The significant positive relationship is consistent with the theoretical relationship between these two variables.

The opposing trends in ANC and pH present a somewhat ambiguous account of the acid-base status of the region's streams. One cannot conclude that streams in the region are clearly acidifying or that acidification is no longer a threat. Instead, we must continue to acknowledge the specific implications of these two variables. Increases in pH demonstrate improvement in the chronic acid-base status of a clear majority of streams. However, the negative trends in ANC at base-poor watersheds confirm the ecological threat imposed by episodic acidification persists for stream biota. More specifically, the pH increases in this study extrapolated over the 25-year timeframe are relatively small when compared to potential changes during acidic episodes. The greatest extrapolated increase is 0.41 pH units, and 86% of sites had a calculated total increase of less than 0.20 pH units. These are minor in comparison to changes in pH during episodic events in SHEN, which have been observed to fall more than 2 units based on in situ measurements (A. Riscassi, personal communication). Therefore, while the overall chronic acid-base status of streams has improved, episodic acidification continues to be a concern for these streams.

Variability of trends in measured analytes within bedrock classes is likely explained in part by mixed bedrock profiles. The classification is based on dominant bedrock (> 50%), allowing for sites to be underlain by multiple bedrock types. For example, a watershed could be underlain 80% by siliciclastic and 20% by mafic bedrock. Although classified in the base-poor siliciclastic group, the base-rich mafic bedrock might disproportionately influence streamwater chemistry. Another uncertainty in bedrock classification is the possible existence of unmapped, but chemically important, carbonate rock inclusions in noncarbonated geologic formations (Sullivan et al. 2007). The presence of carbonate inclusions would dramatically improve the acid-base status of a stream.

4.2 Controls of Bedrock on ANC, SO_4^{2-}, and SBC

The regression of the trends in ANC at sites with increasing or decreasing ANC versus trends in SO_4^{2-} and SBC demonstrate a key difference in the prevailing influence on stream ANC (Figure 4). At sites where increases in ANC have been observed, declines in SO_4^{2-} are contributing more to the increase in ANC than any changes in base cations. Meanwhile, where ANC is experiencing decline, it is the decrease in base cations driving this trend.

This difference can be explained in part by considering the difference in SAC of these bedrock classes. Siliciclastic and mafic sites exhibited greater SO_4^{2-} mobility than felsic watersheds, as demonstrated by higher initial SO_4^{2-} concentration. As such, these sites would be expected to respond to the significant declines in atmospherically deposited SO_4^{2-} before felsic watersheds. With the significantly negative median trend in SO_4^{2-} concentration at siliciclastic and mafic watersheds and no significant median trend in the felsic group, this trend is observed. Retention of SO_4^{2-} and delayed response has been reported previously for catchments with similar soil properties (Alewell et al. 2000; Prechtel et al. 2001) and follows in the conceptual model put forth by Galloway et al. (1983).

With SO_4^{2-} decreasing at siliciclastic and mafic watersheds, base cation availability then appears to determine the direction of change in ANC. One expected result of acidic deposition is the depletion of base cations in watershed soils and associated streams (Fernandez et al. 2003). At sites with a limited base cation supply, the negative effects of this relationship are most magnified. Following this expectation, streams underlain primarily by base-poor siliciclastic bedrock were the only class to exhibit a significantly negative median trend in SBC, which explains the declining ANC. The lack of significant trends in SBC at mafic sites most likely results from the abundant supply of base cations in the soils. Even with decades of elevated acidic input, the supply of base cations has not been depleted in comparison to acidic inputs, leading to minimal change in stream base cation concentration. The facilitated buffering associated with soils with greater base cation content is well documented (Houle et al. 2006; Galloway et al. 1983). No change is expected in the export of base cations from felsic watersheds because acidic loadings have remained relatively constant.

Together, the effects of variations in SO_4^{2-} mobility and base cation supply have driven the trends in ANC in the Ridge/Blue Ridge region. One consequence of this is that sites with the least initial buffering capacity against acidification should also be those most vulnerable to long-term acidification. Similarly, these controls suggest that sites with the greatest initial buffering capacity against acidification would also be the least affected by acidic inputs. The positive relationship between a watershed's initial SBC concentration and the trend in ANC (Figure 5) validates this relationship. Sites with the greatest initial SBC experienced the greatest positive trends in ANC over the study period. Dominated by mafic bedrock, these watersheds owe the greater buffering capacity to their greater base-richness. Meanwhile, at sites that were originally most susceptible to acidification, depletion of the limited supply of base cations has outweighed the effects of declining acidic deposition. The reservoir of base cations in the soil has previously been shown to greatly influence the buffering capacity of surface waters (Houle et al. 2006). Our results extend this relationship to trends in ANC. It is these base-poor sites that are of most concern when evaluating the damaging effects of acidification on aquatic ecosystems. Thus, the continued loss of ANC at these sites because of acidic deposition remains an issue as biota continue to be exposed to harsh chemical environments during episodic acidification events even as sulfur deposition decreases.

4.3 Mass Balance Analysis of Sulfur

The entirety of analyses introduces a critical question concerning the future of these acid-sensitive sites: when will streamwater ANC begin to recover from anthropogenic acidification? For this to occur, the amount of sulfur exported to streams must decrease at a greater rate than base cations. In other words, the ratio of base cation to sulfur input must increase, leading to an increase in ANC. Because the supply of base cations is severely limited at base-poor sites, the mechanism of improved acid-base status will most likely have to center around decreased sulfur input to streams. As noted in this analysis, a major hindrance to increases in ANC in the Ridge/Blue Ridge region is the relatively high SAC in soils compared with other regions affected by acidic deposition. This stored sulfur is predicted to be slowly released into streams over time, providing sulfur in addition and possibly in excess to that of atmospheric deposition (Driscoll et al 1998). Improvements of surface water ANC at base-poor sites is therefore unlikely until this sulfur pool is diminished.

In addressing this issue, the mass balance analysis of sulfur at WOR1 (Figure 7) suggests a potentially optimistic outlook. The analysis reveals net export of sulfur has occurred for the first time in the observed record in the most recent two years. Also of note, net sulfur storage has decreased at a rate of -0.21 kg S ha^{-1} yr^{-1} ($p < 0.01$) over the period of record. If this trend in sulfur storage continues, net export of sulfur should become more frequent in coming years. Following from Mitchell and Likens (2011), with declining inputs from atmospheric sulfur deposition, the relative importance of internal sources of sulfur (i.e. stored) should increase over time. As net export occurs, the reservoir of sulfur stored in watershed soils will decrease, reducing the amount of sulfur available for export to streams. Assuming this site is representative of the larger population of base-poor siliciclastic watersheds, more widespread stabilization or increases in ANC may be approaching in the Ridge and Blue Ridge provinces.

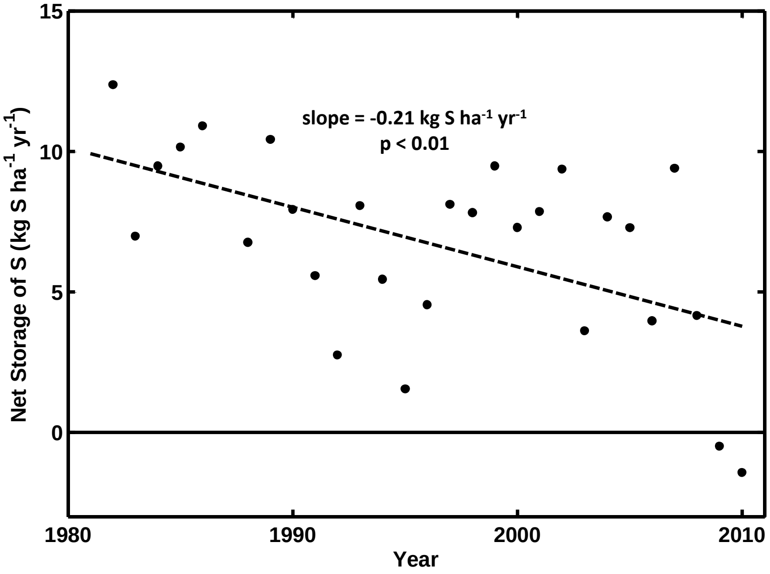

Figure 7: Mass balance analysis of sulfur at WOR1. The calculated total storage is shown for each year of record and the linear regression line is plotted through the data to show the significant decreasing trend.

Even with this potential decline in the reservoir of stored sulfur, increases in ANC are limited by the supply of base cations. Naturally acidifying processes, such as the uptake of base cations by vegetation (Johnson and Todd 1990) or organic matter production and decomposition (Driscoll et al. 1989), impose limitations on this prospect. For example, base cation availability in soils, especially for Ca^{2+}, has been shown to be restricted by vegetative uptake (Johnson et al. 1988). Consequently, biotic controls on base cation supply to these streams complicate the timeline for the stabilization or improvement of streamwater ANC in base-poor systems. Still, the potential for depletion of the stored SO_4^{2-} pool within these watersheds indicates the impact of acid deposition might be diminished in the relatively near future.

5. Conclusion

The responses observed in streams in the Ridge/Blue Ridge region of Virginia to reduced acid deposition over the past 25 years have been markedly dependent on the underlying bedrock of the watersheds. Differences in the SAC and base cation supply at siliciclastic, felsic, and mafic watersheds have led to different trends in SO_4^{2-}, SBC, and ANC. When considering the response of streams in terms of the overall acid-base status, the direction of change in pH and ANC suggest a somewhat ambiguous condition. In absolute terms, the increases in pH across all bedrock classes indicate an improved chronic acid-base status. Nevertheless, the declines in ANC at base-poor watersheds illustrate susceptibility to episodic acidification remains a serious concern for the ecological health of these systems.

Perhaps most interesting, our results indicate that sustained declines in sulfur deposition may lead to general decreases in the pool of stored sulfur in base-poor siliciclastic watersheds. In terms of watershed acidification, the possibility of sulfur export regularly exceeding depositional input represents a noteworthy milestone, where the reservoir of stored sulfur can actually be depleted. Though ultimately limited by the depleted supply of base cations, decreasing the pool of stored sulfur is an important precursor for gradual improvements in streamwater acidity.

The importance of limiting stream acidification is amplified by the emergence of new environmental stressors, especially climate change, which threatens to shrink suitable fish habitat (Flebbe et al. 2006), alter stream chemistry (Evans 2005), and affect the hydrologic cycle (Mitchell and Likens 2011). Significant limitation or reversal of anthropogenic acidification in this region of the U.S. would also represent a major success for federal legislation, specifically the Clean Air Act and amendments, as what was once an exception to the general trend of positive responses to decreased acidic deposition would be eliminated. Continued monitoring and analysis is still needed to monitor this prediction and understand geochemical drivers affecting differences between individual watersheds.

6. Acknowledgements

Support for this study was provided by the U.S. Environmental Protection Agency, the National Park Service, the USDA Forest Service, the Virginia Department of Game and Inland Fisheries, Trout Unlimited, the Appalachian Stewardship Foundation, and NSF grant EAR-0645697. This paper has not been subjected to agency review and no official endorsement by any agency should be inferred. This paper is a contribution to the Shenandoah Watershed Study. We thank Suzanne Maben, Michael Pace, and Karen Rice for their input and help throughout this investigation.

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Chapter 3: Modeling the potential influence of climate change on future watershed acid-base chemistry in Shenandoah National Park, VA using the dynamic biogeochemical model PnET-BGC

Abstract

Although recovery of surface waters from acidification has occurred on a widespread basis across eastern North American and Europe, upland watersheds in the southern Appalachians of the U.S. remain an exception chiefly because of high sulfate (SO_4^{2-}) adsorption has prevented significant acid-base recovery. Projecting the future status of these systems is complicated by anthropogenic climate change, which can act a as a major biogeochemical driver with the potential to alter physical, biological, and chemical processes. We used the biogeochemical model, PnET-BGC, to evaluate the potential effects of future changes in climate on pools, concentrations, and fluxes of major elements at the White Oak Run watershed in Shenandoah National Park, VA. Four global circulation models and two IPCC climate scenarios were utilized in model application. A sensitivity analysis was performed to measure the relative influence of changes in temperature and precipitation on the projections of stream discharge and chemical variables. Stream discharge is expected to increase by 32.7 cm on average over the next century, primarily as a result of increased precipitation. Stream concentrations of SO_4^{2-} and base cations are predicted to decline under all climate scenarios, by 46.6 μeq L^{-1} and 64.4 μeq L^{-1} respectively, while NO_3^- and DOC remain relatively constant over the 21st century. Altogether, the decline in base cations is projected to outpace that of SO_4^{2-}-, reducing stream alkalinity overall. The effects of changes in temperature and precipitation on stream chemistry are primarily manifested through dilution of soil and surface waters, increased plant demand for nutrients, and increased rates of decomposition mineralization. On average, projected climate change is expected to deteriorate watershed alkalinity more so than what would be expected

under a static climate, indicating another significant negative consequence of this global problem.

1. Introduction

Acid deposition has been a major global biogeochemical driver for decades, adversely affecting aquatic ecosystems across the U.S. and Europe (Stoddard et al., 1999; Kahl et al., 2004; Driscoll et al., 2007). The deleterious effects of acidic streamwater are well established, most notably the loss of fish, macroinvertebrates, and other aquatic species in acid sensitive systems (Schindler, 1988; Driscoll et al., 2001). As acid deposition in the U.S. has declined as a result of the Clean Air Act and associated amendments (CAAA), the concern imposed by acid deposition is waning (Chestnut and Mills, 2005). One major exception to this general pattern is in the mountainous regions of western Virginia, where stream acidification in the base-poor watersheds continues despite the significant decrease in acid deposition (Webb et al., 2004; Skjelkvåle et al., 2005; Robison et al., 2013).

The key feature distinguishing this region's biogeochemical response from other areas of the U.S. is the high sulfate (SO_4^{2-}) adsorption capacity of watershed soils (Church et al., 1990; Herlihy et al., 1993), a result of not being affected by the most recent glaciation (Reuss and Johnson 1986; Rochelle et al. 1987). Elevated sulfur retention in watershed soils has delayed and limited major changes in stream chemistry (Church et al., 1990; Herlihy et al., 1993; Robison et al., 2013), while also ensuring a legacy of sulfur in streams as the stored pool is slowly released (Sullivan et al., 2008).

One major consequence of this history of acidic deposition and SO_4^{2-} storage has been the decline of acid neutralizing capacity (ANC) in the region's upland surface waters (Cosby et al., 2004; Robison et al., 2013). ANC, the measure of an unfiltered water sample to neutralize strong acid inputs, is a critical indicator of ecological vulnerability to acidification (Lien et al., 1996; Wigington et al., 1996; Kowalik and Ormerod, 2006). ANC can be defined as charge balance ANC (Cosby et al., 2001), here referred to as calculated alkalinity (CALK). Under this definition, CALK is defined as the equivalent sum of base cation concentrations (Ca^{2+}, Mg^{2+},K^{+}, and Na^{+}, NH_4^{+} ; SBC) minus the equivalent sum of strong acid anion concentrations (SO_4^{2-}, NO_3^{-}, and Cl^{-}; Reuss and Johnson, 1986). With acid deposition expected to decline over the next century (Dentener et al., 2006), a corresponding increase in CALK could be reasonably expected.

A factor complicating the chemical outlook of these systems is anthropogenically-driven climate change as a major biogeochemical driver. The ongoing and future impacts of climate change are likely to vary across the globe, but universally they have substantial implications for biogeochemical cycling, including the response of ecosystems to acid deposition (Murdoch et al., 1998; Murdoch et al., 2000 Boisvenue and Running, 2006). Predicting the interaction of climate change and acidification is difficult because of their complex temporal and spatial relationship and the high uncertainty of future emissions of CO_2, sulfur, and nitrogen (Campbell et al., 2009; McLaughlin and Percy, 1999). Many variables affected by climate change may exacerbate or ameliorate the rate and degree of acidification and recovery, both with respect to chemical as well as biological effects. Chief among these that directly influence acid-base processes are increased temperature (Rustad et al., 2000; White et al., 1999) and an altered hydrological cycle (Boisvenue and Running, 2006; Kleinman et al., 2006).

The mechanisms of interaction between climate and acidification effects are still, however, poorly understood and need further examination. The complexity of the interaction suggests this may be best accomplished through the use of dynamic models (Aber et al., 2001).

This study explores the biogeochemical interaction of atmospheric deposition and climate change over the next century at a long-term monitored watershed in Shenandoah National Park, VA (SHEN) using the fully integrated hydrologic and biogeochemical model PnET-BGC and statistically downscaled climate projections. PnET-BGC accounts for a) major element cycling such as carbon, sulfur, nitrogen, and base cations; b) water cycling and demand; and c) biotic inputs, including changes in forest productivity, plant demand for nutrients, and decomposition rates (Gbondo-Tugbawa and Driscoll 2001; Pourmokhtarian et al., 2012).

Specifically, the objectives of this are to investigate (1) how climate change will affect recovery from acidification as a result of decreased acidic deposition and (2) identify the processes through which this interaction will be manifested (e.g. mineral weathering, SO_4^{2-} adsorption, etc.) Following model application and calibration, a detailed evaluation of the response of surface water chemistry was performed for variable climate scenarios. The analysis focuses on long-term evaluations of solute concentrations.

2. Site Description

The watershed considered in this study is White Oak Run (WOR1), which is located in the uplands of the Blue Ridge physiographic province within SHEN (Figure 1). WOR1 been studied as a part of the Shenandoah Watershed Study program (http://swas.evsc.virginia.edu), with weekly stream chemistry and temperature measurements and daily discharge measurements dating back to 1979. Although the area's land use history includes agriculture, timber harvesting, and human habitation, this activity ceased upon establishment of the national park in 1935 (Fievet et al., 2003). Natural disturbance has been limited, with the exception of a defoliation event associated with a gypsy moth outbreak beginning in the late 1980's (Webb et al., 2004, Webb et al., 1995). Watershed land cover is dominated by deciduous forest (Virginia Dept. of

Forestry, 2005), and was represented in the model by the northern hardwood forests described in previous PnET-BGC applications (Aber and Federer, 1992).

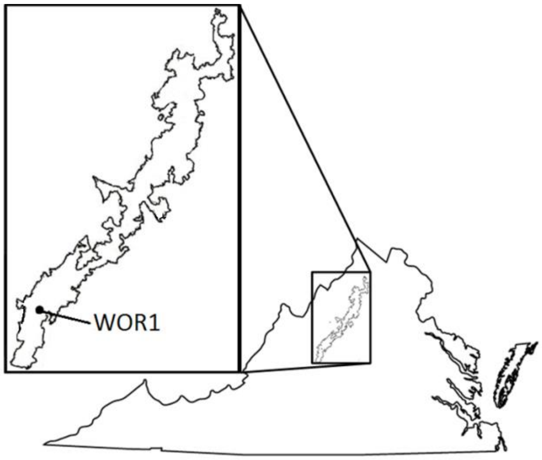

Figure 1: Location of WOR1 within Shenandoah National Park, VA (38.25^o, -78.75^o).

3. Methods

3.1 Model Description

PnET-BGC is an integrated biogeochemical model designed to simulate the response of forested ecosystems to changes in atmospheric deposition, land disturbance, and climate. Detailed descriptions of the processes and calculations included in the model have been reported previously (Aber and Federer, 1992; Aber et al, 1996, 1997; Gbondo-Tugbawa et al., 2001). PnET-BGC performs exceptionally well in small, high-elevation watersheds where detailed data are available for inputs and parameter values (Chen et al 2004; Chen and Driscoll 2005; Zhai et al., 2008; Wu and Driscoll, 2009; Driscoll et al., 2013).

While other models (e.g., MAGIC [Cosby et al., 2001], ILWAS [Gherini et al., 1985]). could be used to simulate climate effects on biogeochemical cycling, these models either do not directly include biotic processes or have large input requirements (Gbondo-Tugbawa et al., 2001). Major biotic and abiotic processes are represented in PnET-BGC, including atmospheric deposition, canopy interactions, CO_2 fertilization, litterfall, forest growth, root uptake, snowpack accumulation and loss, soil organic matter dynamics, nitrogen mineralization and nitrification, mineral weathering, chemical reactions involving solid and solution phases, and surface water processes.

3.2 Data Sources and Inputs

Inputs required for PnET-BGC include climatic data (solar radiation, precipitation, and temperature), atmospheric deposition of base cations, SO_4^{2-}, nitrate (NO_3^-), and chloride (Cl^-), vegetation type, element stoichiometry of biomass, soil characteristics, element primary weathering rates, soil exchange and adsorption coefficients, and historical land disturbance. Much of this information is already available for these watersheds from direct measurement (http://swas.evsc.virginia.edu) or can be adopted from previous PnET-BGC applications to other watersheds (Aber and Federer, 1992; Aber et al, 1996, 1997; Gbondo-Tugbawa et al., 2001; Pourmokhtarian et al., 2012).

Wet deposition for base cations, SO_4^{2-}, NO_3^-, and Cl^- for Big Meadows in SHEN (VA28) was obtained from the National Acidic Deposition Program for the period 1981-2012 (NADP, 2013). The ratio of wet to dry deposition for each ion was collected from the Community Multiscale Air Quality model (CMAQ; Byun and Ching, 1999). The methodology used for estimating deposition inputs for the period between 1000 A.D. and the beginning of measured data is based on Chen et al. (2004). Briefly, for the period 1000 to 1850, the background deposition is assumed to be 10% of the current deposition. Deposition inputs after 1850 are then assumed to increase linearly until 1900. Wet deposition of SO_4^{2-} and NO_3^- from 1900 to 1981 was estimated from the empirical relationships between current estimates of sulfur dioxide (SO_2)

and nitric oxides (NO_x) emissions and the measured precipitation chemistry (Driscoll et al., 2001, 2003). A similar strategy was used to estimate the historic deposition of base cations and Cl^- using empirical relationships between particulate matter (PM-10) emissions and precipitation chemistry. Historical emission data for SO_2, NO_x, and PM-10 was obtained from U.S. EPA compilation of emission of Criteria Air Pollutants (Nizich et al., 1996).

Daily precipitation and temperature minimum and maximum estimates for WOR1 from 1900-2012 were collected from PRISM (Parameter-elevation Regressions on Independent Slopes Model), an approach to mapping climate that seeks to combine the strengths of human-expert and statistical methods (Daly and Neilson, 1992; Daly et al., 1994; 1997; 1998; Daly and Johnson, 1999; Johnson et al., 2000). Solar radiation data is available for Big Meadows, VA over the period 1988-2012 from the EPA Clean Air Status and Trends Network (CASTNET, 2013). Big Meadows is located in SHEN 40 km northwest of WOR1. Solar radiation was adjusted to WOR1 based on latitude following methods used in previous PnET applications (Aber and Federer, 1992; Driscoll et al., 2001; Pourmokhtarian et al., 2012). Radiation is input as photosynthetically active radiation (PAR; $\mu mol\ m^{-2}\ s^{-1}$) into PnET.

Soil input parameters for PnET-BGC, such as mineral weathering, were informed by values used in the MAGIC model on watersheds in this area (Cosby et al., 2001). Vegetation cover is available from the Virginia Department of Forestry (2005). PnET-BGC characterizes vegetation using the major cover types represented in the study and the element stoichiometries associated with these cover types. This information and other general vegetation parameters, including photosynthesis and carbon allocation, have been reported for similar forest types in previous studies (Aber et al., 1995; Driscoll et al., 2001; Ollinger et al., 2002).

3.3 Future Climate Scenarios

A standard downscaling routine (Hayhoe et al., 2007, 2008; Liang et al., 1994; NECIA, 2006) was applied to four atmosphere-ocean general circulation models (AOGCMs) to generate monthly temperature, precipitation, and solar radiation at 1/8° resolution for the period of 1950 to 2100 for WOR1. The models used in this study are the NCAR Community Climate System, version 4 (CCSM4), the United Kingdom Meteorological Office Hadley Centre Earth System Model, version 2 (HadGEM2), the Model for Interdisciplinary Research on Climate, version 5 (MIROC5), and the Meteorological Research Institute Coupled GCM (MRI-CGCM3). A detailed description, comparison, and validation of the AOGCM downscaling method is provided by Campbell et al. (2011), Hayhoe et al. (2004, 2007, 2008), and NECIA (2006).

The IPCC Special Report on Emissions Scenarios (Nakićenović et al., 2000) A1fi and B1 scenarios were utilized to represent possible higher- and lower-emission futures, respectively. At the end of the 21st century under these two scenarios, concentrations of atmospheric CO_2 are estimated to triple (970 ppm for A1fi) and double (550 ppm for B1) preindustrial conditions. Model predictions of mean air temperature estimate average increases of 2.67 °C for the B1 climate scenarios and 5.32 °C for the A1fi scenarios, while annual precipitation increases were 14.3 cm and 40.9 cm for the B1 and A1fi scenarios respectively (Table 1) by the end of the century (2071-2100) compared to the most recent three decades of observation (1981-2010).

Atmospheric deposition of all ions was set at 90% of the average ion concentration over the period 2001-2010. Declines in atmospheric deposition are generally expected by emission and deposition models, but the magnitude of decline is uncertain (Pye et al., 2009; Dentener et al., 2006). Because the central objective of the paper is to examine potential effects of climate change on the acid-base chemistry of a watershed, the absolute values of atmospheric deposition are not considered to be as crucial as climatic variables. By including a slight decline in atmospheric inputs of ions, we can capture the general trend predicted over the next century. The effect this choice has on results is considered in discussion.

Table 1: Predicted changes in climate variables for each AOGCM and climate scenario for WOR1, comparing average values from 1981-2010 to 2071-2100.

AOGCM	Climate Scenario	T_{Max} (^oC)	T_{Min} (^oC)	Precipitation (cm)	PAR (μmol m^{-2} s^{-1})
CCSM4	A1fi	5.26	3.90	37.2	23.9
	B1	2.65	1.71	17.6	26.9
HadGEM2	A1fi	7.34	8.18	29.1	43.0
	B1	4.13	2.79	8.52	38.6
MIROC5	A1fi	5.89	5.65	34.4	61.7
	B1	3.58	3.20	20.6	52.1
MRI-CGCM3	A1fi	3.12	3.2	62.8	7.93
	B1	1.74	1.52	10.4	13.0

3.4 Model Implementation

Model application and evaluation follows that of Pourmokhtarian et al. (2012), which includes a spin-up period (1000-1850), a period of hindcast simulations (1850-2010), and the downscaled forecasted data (2011-2100). To examine the relative impacts of changes in temperature and precipitation on the acid-base chemistry of the stream, a range of temperature and precipitation ramps over the period 2011-2100 were applied in the model. These ramps are referred to by the change in average annual temperature and precipitation over the 21st century, and the upper bounds were determined by the change expected in the A1fi scenario. Temperature ramps ranged from no change to an increase of 6 ^oC at 1 ^oC intervals, and precipitation ranged from no change to an increase 60 cm at 15 cm intervals. Applying every combination of these ramps resulted in 25 combinations of temperature and precipitation scenarios. The climate scenario with no change in precipitation or temperature was considered the static climate scenario, used as a reference case to isolate the effects of climate change.

To account for the gypsy moth defoliation events of the late 1980's (Webb et al., 1995), a disturbance regime was included in the model. Disturbance intensity and biomass removal were adjusted to optimize the statistical fit of the model projected stream NO_3^- concentration during the years of and following disturbance (1990-1998).

3.5 Statistical Measure of Model Fit

In applying PnET-BGC to a new region, the necessity of model calibration is amplified. Calibration of discharge and stream chemistry was used in this evaluation. Two statistical indicators were used to evaluate model performance of stream chemical variables: normalized mean error (NME) and normalized mean absolute error (NMAE) (Janssen and Jeuberger, 1995; Pourmokhtarian et al., 2012). NME provides a comparison for the means of predicted and observed values and is an index of relative bias, indicating overestimation (NME > 0) or underestimation (NME < 0) of simulations. The NMAE indicates any discrepancy between model simulations and observed values. The smaller the NMAE, the closer the model simulations are to observed values. For hydrological comparison, the Nash-Sutcliffe efficiency index was used. The Nash–Sutcliffe efficiency index is a widely used and reliable statistic for assessing the goodness of fit of hydrologic models (McCuen et al., 2006). Nash–Sutcliffe efficiencies can range from $-\infty$ to 1, with an efficiency of 1 indicating to a perfect fit of modeled data to the observed discharge. An overlapping period of model output and measured data was used in error calculation, 1980-2010 for most variables. For DOC, consistent measurement did not start until 1995; and for NO_3^-, the period 1990-1997 was not considered in fit analysis because of large disturbance in concentrations which resulted from the gypsy moth defoliation.

3.6 Model Adjustments

Two adjustments were made to PnET-BGC in this application. First, a new SO_4^{2-} adsorption routine was included to account for the elevated adsorption capacity typical of soils in the southern Appalachians. A nonlinear Langmuir isotherm was included to account for the dependence of SO_4^{2-} adsorption on SO_4^{2-} concentration:

$$\mathrm{SO_4^{2-}Adsorption} = \frac{\mathrm{E}_{Max} * [\mathrm{SO_4^{2-}}]}{\mathrm{E}_{Half} + [\mathrm{SO_4^{2-}}]} \quad (1)$$

where E_{max} (mol kg^{-1}) is the maximum adsorption capacity and E_{Half} (μeq L^{-1}) is the half saturation constant. Values for E_{max} and E_{Half} were initially informed from soil properties measured by Ingersoll (1994) and were further adjusted through model calibration.

Secondly, an in-stream NO_3^- removal term was added following the work of Scanlon et al. (2010) in SHEN, who showed that denitrification and biotic uptake can account for the removal of more than 90% of the NO_3^- that enters the stream network before it reaches the watershed outlet. Based on estimates from a neighboring watershed, this takes the form of:

$$(2) \quad P_{Removal} = P_{Max} * \exp(-B * NO_3^- \; Flux)$$

Percent removal ($P_{Removal}$) is a function of nitrate flux, where P_{Max} (%) is the maximum percent removal and B (s mg^{-1}) is a constant relative to the watershed. These values were derived directly from observations made by Scanlon et al. (2010) at a nearby watershed.

4. Results

4.1 Model Evaluation and Parameterization

Model inputs were determined by minimization of error metrics. The model was initially run with parameters informed from previous studies in the region. Based on the fit of model output, parameters were adjusted accordingly, including water holding capacity, weathering rates, and SO_4^{2-} adsorption terms. Briefly, initial values from previous studies were used to initiate the model (e.g. SO_4^{2-} adsorption terms from Ingersoll [1994]), and then adjusted to minimize statistical error. Select input parameters determined through calibration are listed in Table 2. Calibration of annual output of PnET-BGC to measured values resulted in satisfactory fit (Table 3).

Table 2: Key model input parameters determined for WOR1 through model calibration. $^{*}NO_3^-$ removal terms were not calibrated, but adapted directly from Scanlon et al. (2010).

Variable	Value
Water holding capacity (cm)	38
Weathering (mg m^{-2} mo^{-1})	
Ca	13.7
Mg	22.0
K	4.2
Na	0.8
Sulfate adsorption	
E_{Max} (mol kg^{-1})	0.045
E_{Half} (μeq L^{-1})	350
NO_3^- removal*	
P_{Max} (%)	91.9
B (s mg^{-1})	0.0339

Table 3: Summary of annual model performance metrics normalized mean error (NME) and normalized mean error (NMAE) over the period 1980-2010 for SO_4^{2-}, SBC and CALK. The same period without the consideration of 1990-1998 was utilized for NO_3^- to minimize the effects of a forest disturbance. For DOC, observations were not consistently made until 1995, thus the period of comparison is 1995-2010.

Variable	NME	NMAE
SO_4^{2-}	0.03	0.08
NO_3^-	-0.12	0.62
SBC	-0.06	0.04
CALK	-0.09	0.14
DOC	-0.02	0.18

Predicted stream discharge results in a relatively high Nash-Sutcliffe efficiency index (0.76), indicating the model represents the general patterns of streamflow well (Figure 2a). Model predictions of stream SO_4^{2-} concentrations fit well with observed values over the compared time period (NME = 0.03, NMAE = 0.08; Figure 2b), with the exception of the decrease in SO_4^{2-} concentration associated with the gypsy moth defoliation event in the early 1990's. The model did accurately account for this disturbance in NO_3^- concentrations. The poor overall statistical fit of the model to observed data (NME = -0.12, NMAE = 0.62; Figure 2c) is due in large part to the low concentrations characteristic of WOR1, which amplify error in the NME and NMAE metrics. Excluding the years immediately following the gypsy moth disturbance, the difference between modelled and observed concentrations of NO_3^- were never greater than 5µeq L^{-1}. SBC concentrations predicted by PnET-BGC fit observed data well (NME = -0.06, NMAE = 0.04; Figure 2d), including the increase in concentrations following the gypsy moth disturbance. The mean predicted concentration of DOC was acceptable (NME = -0.02), but overall fit was not ideal (NMAE = 0.18; Figure 2e). Error was again magnified by the low concentrations observed, and the maximum difference in observed and predicted DOC concentration was low (0.33 mg L^{-1}). CALK calibration exhibited a comparatively high level of error (NME = -0.09, NMAE = 0.14; Figure 2f). By definition, CALK includes all acid anions and base cations in its calculation. As such, any errors included in the model predictions for those ions will also be included in the predictions for CALK. Of particular influence are the lack of accounting for gypsy moth disturbance's effect on SO_4^{2-} concentrations and the combined underestimation of SBC and overestimation of SO_4^{2-} and NO_3^-.

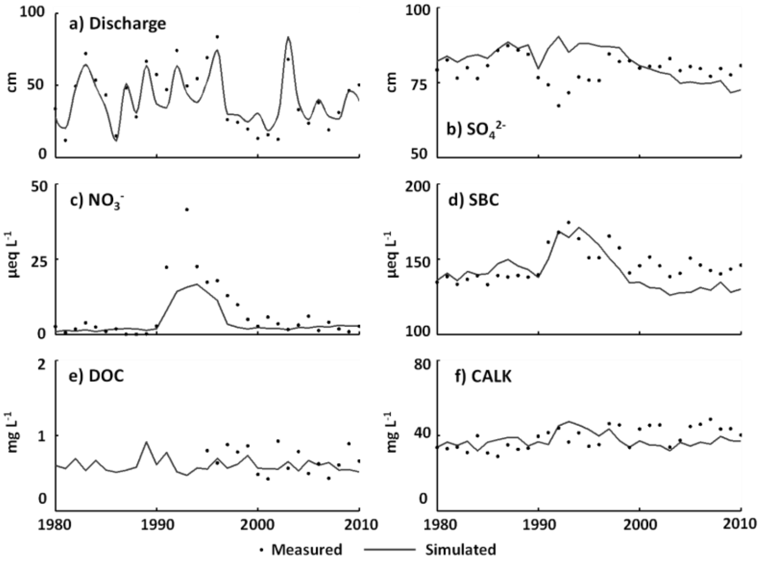

Figure 2: Comparisons of measured and simulated values of a) discharge, b) SO_4^{2-}, c) NO_3^-, d) SBC, e) DOC, and f) CALK over the period 1980-2010 at WOR1. Consistent DOC observations did not begin until 1995.

4.2 Model Predictions

Model predictions comparing average values for the period 1981-2010 for discharge, SO_4^{2-}, NO_3^-, SBC, CALK, and DOC under each AOGCM and climate scenario are listed in Table 4 and depicted in Figure 3. To briefly summarize these results, stream discharge is projected to increase under all scenarios, with an average increase of 32.7 cm under A1fi scenarios, and 4.2 cm under B1 scenarios. The concentration of SO_4^{2-} is projected to decrease under all scenarios, with an average decline of 46.6 μeq L^{-1}. NO_3^- concentrations remain relatively low under all simulations (mean change = 0.03 μeq L^{-1}), with the largest change predicted to be 2.06 μeq L^{-1} (CCSM4 A1fi). All model applications predict a decline in SBC, with A1fi climate scenarios projecting a greater mean decline (70.5 μeq L^{-1}) than the B1 scenarios (58.2 μeq L^{-1}). DOC exhibits little change in concentration (mean change = -0.06mg L^{-1}), increasing only in the MRIOC5 projections. Finally, CALK decreased under all model applications except the CCSM4 A1fi, with mean changes under the A1fi (-9.98 μeq L^{-1}) and B1

(-6.34 μeq L^{-1}) being remarkably close. Stream discharge and chemistry are also expected to change under a static climate (Table 4). Discharge (2.28 cm) and DOC (0.06 mg L^{-1}) increased slightly under a static climate, while concentrations of SO_4^{2-}, NO_3^-, SBC, and CALK all declined.

Table 4: Predicted changes in stream variables at WOR1 by each AOGCM climate scenario and a static climate scenario, determined by comparing average values from 1981-2010 to those in 2071-2100. The average initial NO_3^- concentration does not include the years 1990-1998 to minimize the influence of the gypsy moth disturbance.

Variable	Static Climate	CCSM4		HadGEM2		MIROC5		MRI-CGCM3	
		A1fi	*B1*	*A1fi*	*B1*	*A1fi*	*B1*	*A1fi*	*B1*
Discharge (cm)	2.28	15.7	3.60	36.2	4.85	21.0	9.53	58.0	1.16
SO_4^{2-} (μeq L^{-1})	-44.0	-46.3	-44.1	-47.7	-42.9	-45.9	-47.6	-56.2	-42.2
NO_3^- (μeq L^{-1})	-3.01	2.06	1.79	-1.20	-0.39	1.28	-1.14	-1.26	1.65
SBC (μeq L^{-1})	-58.3	-53.0	-50.5	-73.6	-61.9	-71.9	-71.8	-83.6	-48.8
CALK (μeq L^{-1})	-6.36	0.95	-0.38	-13.2	-10.2	-15.1	-14.0	-12.6	-0.81
DOC (mg L^{-1})	0.06	-0.09	-0.07	-0.27	-0.13	0.04	0.09	-0.01	-0.09

The dynamics predicted over the next century are consistent between the AOGCMs, with minor exceptions (Figure 3). In terms of SO_4^{2-}, the majority of decline is expected in the early part of the century, followed by stabilization towards the end of the century. The concentrations of NO_3^- and DOC are projected to remain relatively constant throughout the century, while base cations are predicted to decline steadily. Finally, CALK is projected to increase towards midcentury, before declining and then stabilizing by the end of the century.

5. Discussion

5.1 Sensitivity Analysis

Under the climate scenarios utilized in this application, PnET-BGC projects that discharge at WOR1 will most likely increase over the next century. This is caused predominantly by increased precipitation expected under all future climate scenarios. This is offset to some extent by the projected changes in temperature. As temperature increases, so will evapotranspiration, decreasing the amount of water available for streamflow. Similarly, increases

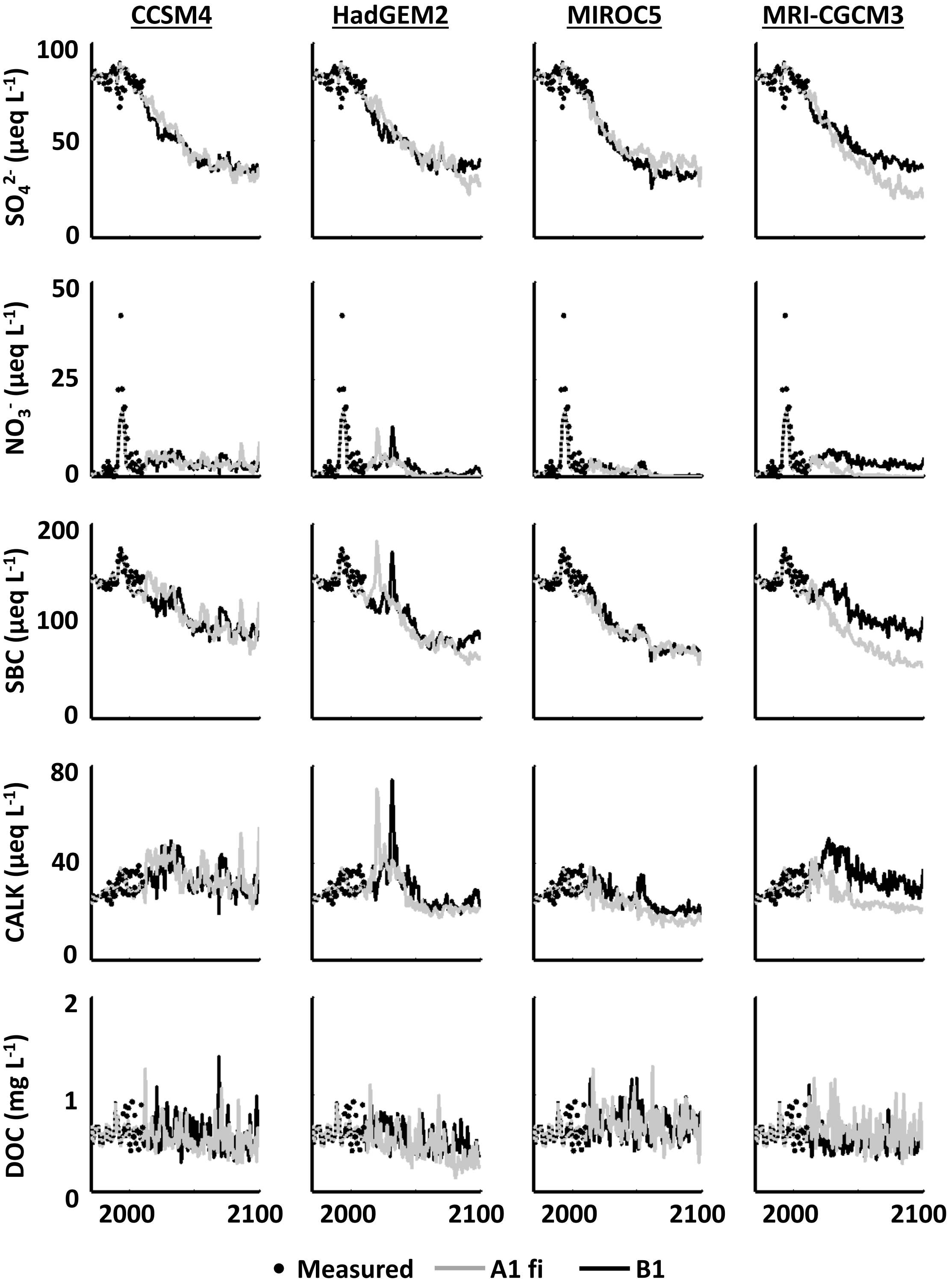

Figure 3: Projected and observed annual concentrations of SO_4^{2-}, NO_3^-, SBC, CALK, and DOC at WOR1 over the period 1950-2100 under each AOGCM A1fi and B1 climate scenario.

in temperature and PAR increase the growth efficiency of plants in general, raising transpiration rates. However, this temperature effect is minor in comparison to the influence of changes in precipitation.

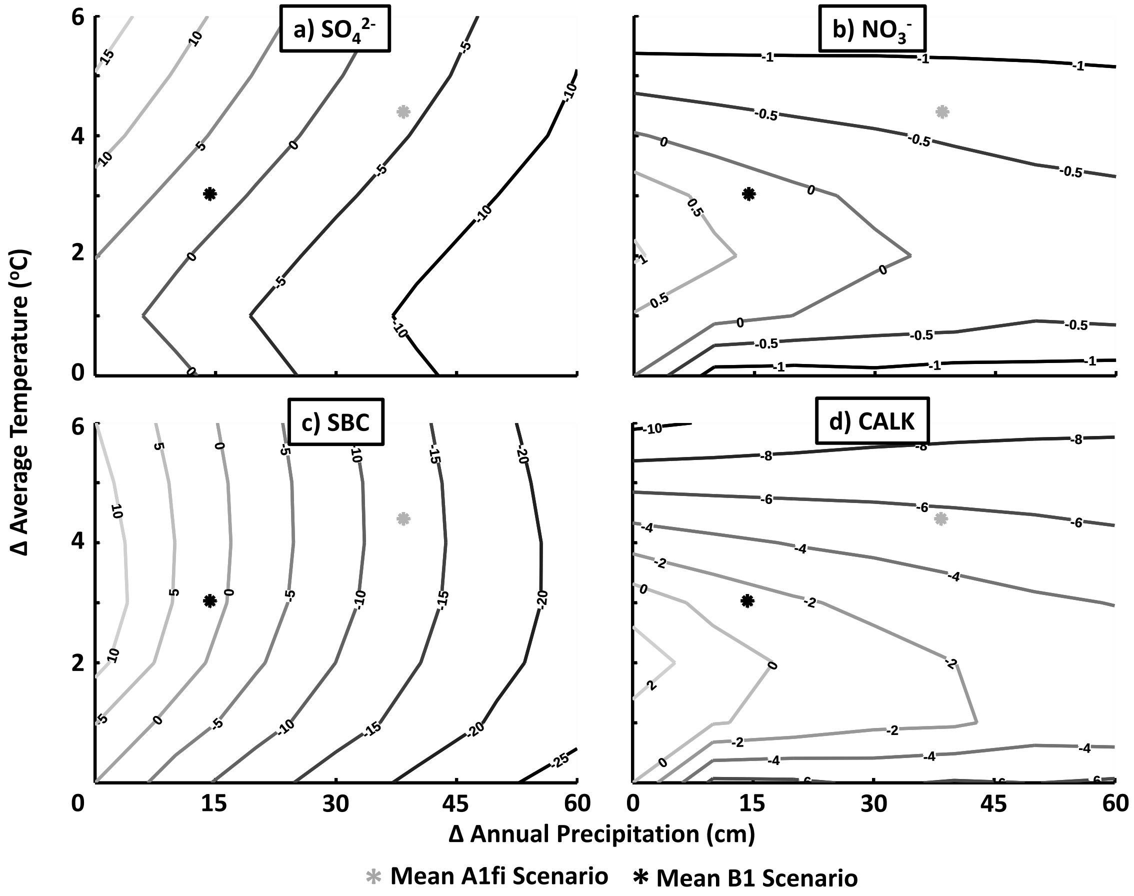

Figure 4: Contour plots illustrating the relative influence of changes in precipitation and temperature on the change in stream a) SO_4^{2-}, b) NO_3^-, c) SBC, and d) CALK relative to a static climate. The origin represents the static scenario and is set to 0 μeq L^{-1}. Contour lines are measured in μeq L^{-1}.

Analysis of the relative impacts of increases in temperature and precipitation on selected stream chemistry variables for WOR1 in PnET-BGC reveals an array of interactions, unique for each variable. For SO_4^{2-} (Figure 4a), the change in stream concentration appears to be influences primarily by changes in stream discharge. At elevated precipitation levels, discharge increases while the supply of SO_4^{2-} remains relatively constant. In combination, this leads to dilution of

SO_4^{2-}, or more simply a decline in concentration. At high temperatures, evapotranspiration increases, reducing streamflow and ultimately increasing the concentration of SO_4^{2-}. Because of the interplay of temperature and precipitation in affecting stream discharge, SO_4^{2-} concentration displays dependence on both these variables.

Sulfur dynamics are also affected in the model to some degree by changes in vegetation growth and decomposition. This effect is less influential because the pool of sulfur in vegetation is much less affected by changes in climate than the soil pool and as such discharge exerts a greater control on SO_4^{2-} dynamics. At WOR1, SO_4^{2-} mobility has been shown to be controlled predominantly through soil adsorption (Robison et al., 2013; Sullivan et al., 2008). In turn, soil adsorption is influenced by hydrology (Mitchell and Likens, 2011). As deposition of SO_4^{2-} declines, precipitation and thus soil water becomes relatively more dilute, allowing for SO_4^{2-} desorption and depletion of the soil pool. Soil adsorption is also relatively independent of temperature, especially on the scale of projected climate scenarios (Singh, 1984). The model prediction showing strong hydrological influences follows this set of expectations. For example, although the MRI-CGCM3 model projects moderately similar temperature changes under the A1fi (3.2 ^{o}C) and B1 (1.6 ^{o}C) scenarios, the increase in precipitation is 50 cm greater for the A1fi scenario. In examining this effect on SO_4^{2-} (Figure 5), the soil pool is depleted more so in the A1fi application.

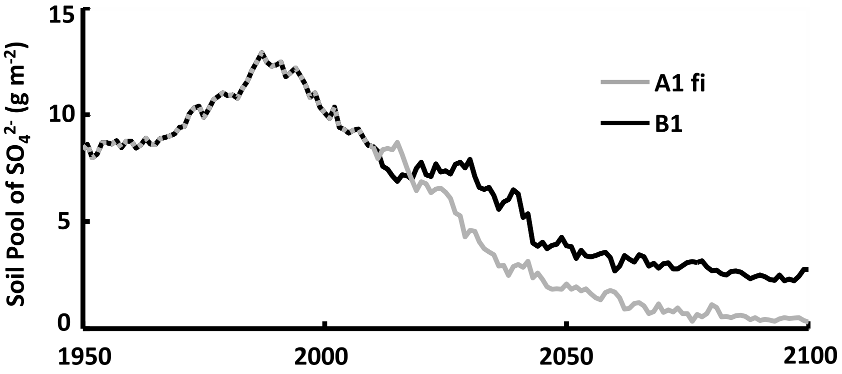

Figure 5: MRI-CGCM3 projections of the soil pool of SO_4^{2-} at WOR1 over the period 1950-2100.

Meanwhile, the change in concentration of NO_3^- exhibits much stronger dependence on temperature (Figure 4b). With increases in temperature, the rate of nitrogen mineralization and nitrification increases, providing more NO_3^- to the stream. However, temperature increases also elevate plant demand, reducing the available pool of base cations. Furthermore, organic matter decomposition increases with temperature, and a reduction in the organic matter pool reduces the available pool for mineralization over the long-term. The interplay of these processes dominates the magnitude of change in NO_3^- concentration. At slight increases in temperature (1-2^{o}C), the change in mineralization and nitrification rates is more substantial, leading to increased concentrations of NO_3^-. At larger increases in temperature, plant demand and organic matter decomposition increases enough to deplete the soil pool, leading to a decline in stream SBC concentration. The influence of precipitation on the change in NO_3^- concentration is similar to that affecting SO_4^{2-} concentration, but is much slighter because little nitrogen in the system is found within the soil pool, preventing dilution effects to have a large influence.

The dependence of plant growth, organic matter decomposition (Kirschbaum, 1995), and mineralization on temperature in general are well-documented (Knoepp and Voss, 2007; Knoepp et al., 2008). Furthermore, at WOR1, NO_3^- has been shown to be much more closely associated with vegetation dynamics than with changes in the inorganic soil pool (Eshleman et al., 1998). These influences on nitrogen dynamics are accurately described by the model results.

The contour plot for SBC suggests that precipitation has a stronger influence than temperature (Figure 4c). On closer investigation, the interplay of temperature and precipitation in governing stream SBC becomes more apparent. First, the change in concentration of SBC is in part controlled by discharge in a very similar way to SO_4^{2-}, with dilution greatest at high precipitation and low temperature increases. Underlying this relationship is a dependence on temperature similar to NO_3^-. As shown by the MRI-CGCM3 A1fi simulation, as temperature increases, so does total plant assimilation (Figure 6a) and organic matter decomposition (Figure 6b). As the soil pool of organic matter is depleted mineralization is limited and ultimately wanes. Because large increases in temperature have opposing effects on the direction of change in SBC in terms of discharge (increased SBC) and vegetation demand (decreased SBC) are opposed, the changes cancel out to some extent, concealing the temperature influence in the contour plot.

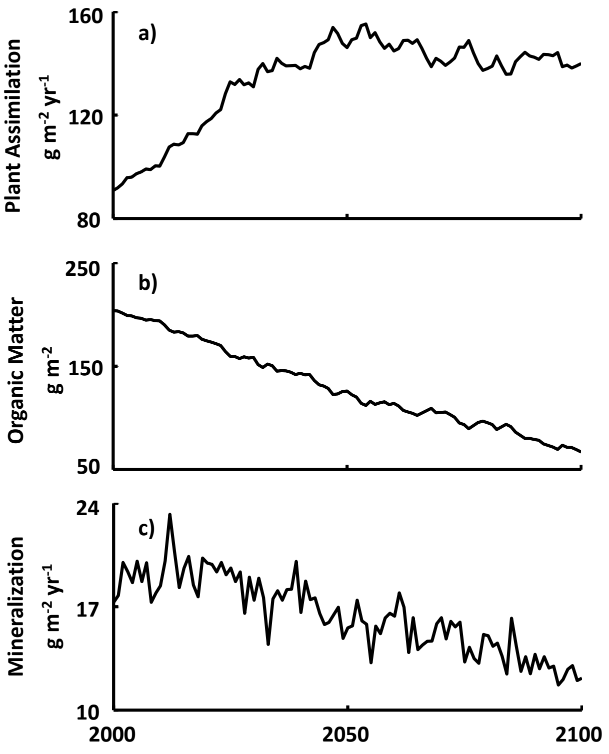

Figure 6: Projections for a) the plant assimilation of base cations, b) the organic matter pool of base cations, and c) the mineralization of base cations at WOR1 in the MRI-GCM3 A1fi model simulation over the period 1950-2100.

Comparatively, base cations are related to changes in vegetation growth and decomposition, but even more so by hydrology because of the large soil pool (Rice and Bricker, 1995). Mineral weathering acts as the primary source of base cations to the watershed. In PnET-BGC, the rate of mineral weathering is not dependent on temperature or precipitation, so this source remains throughout model simulations regardless of climate scenario (Velbel, 1993; Kump et al., 2000). Nonetheless, the pool of base cations remains susceptible to depletion as a result of increased drainage. The dependence of stream SBC on both hydrology and vegetation dynamics in PnET-BGC match these assumptions. The larger changes exhibited by SBC relative to SO_4^{2-} and NO_3^- is simply a result of the larger pool and initial concentration.

The contour plot for CALK appears similar to that of NO_3^- (Figure 4d), yet the magnitude of variation observed for CALK are much greater than those observed for NO_3^-, thus the combined impact of other constituents must explain this response. By definition, CALK is the difference between base cations and acid anions, so the changes in SO_4^{2-} and SBC must be considered to understand the dynamics of CALK. As described earlier, the dominant process affecting the change in SO_4^{2-} and SBC is variation in discharge. This dependence of SO_4^{2-} and SBC on discharge is nearly equivalent, essentially eliminating the influence of drainage in terms of CALK. This leaves the vegetation, organic matter, and mineralization dynamics described for NO_3^- and SBC to act at the determinant influence on changes in CALK, which is observed. Thus, although the observed influence on CALK in this model application is predominantly temperature, it is really the totality of all these processes that ultimately controls stream alkalinity.

5.2 Influence of Climate on the Acid Base Trajectory

Even under a static climate, PnET-BGC projects that WOR1 will experience as overall loss of alkalinity by the end of the current century. Both SO_4^{2-} and SBC are expected to decline to some extent because of decreasing depositional inputs from peak levels in the 1970's, but the observed decrease in streamwater SBC is projected to outpace that of SO_4^{2-} over the long-term, causing CALK to decline. This difference is a result of the influence of both drainage and vegetative demand on the available soil poof of base cations. Dilution as a result of increased discharge will have similar effects on both SO_4^{2-} and SBC. However, base cations are found in larger proportion in vegetation and organic matter compared to SO_4^{2-}, thus indicating that the temperature influences on these processes will have a greater influence on SBC than on SO_4^{2-} and the long term declines in the stream concentration of base cations will generally be larger.

Comparing this static climate scenario to projected climate change scenarios utilized in this study, alterations in climate will on average enhance the decline in CALK (Figure 4d).

Under the average A1fi scenarios, this is manifested primarily through increased loss of SBC as a result of increased plant demand. The higher temperatures associated with this climate scenarios result in more plant growth, a higher base cation demand, and therefore less available base cations. The average difference in CALK between the static climate scenario and the average B1 scenario is less than 1 μeq L^{-1}. Under the B1 scenario, temperature increases are relatively moderate, allowing for increased mineralization rates to balance decreases from plant demand and dilution. Nevertheless, the reduction of CALK is still greater under this scenario, indicating even this smaller climate change scenario may have negative consequences for stream alkalinity.

5.3 Context and Implications

Prior to this investigation, studies of future scenarios of acidification and recovery in the southern Appalachians have been limited to alterations in deposition (Sullivan et al., 2007). Although this process is critical to the future acid-base status of these systems, ignoring the effect of climate change makes projections dubious (Campbell et al., 2009). The results presented here suggest that climate change will have wide ranging effects on watershed chemistry at WOR1, which interact with the acid-base chemistry in diverse ways. Direct chemical and biological effects of climate change appear to be centered on biological cycling and transformation, namely mineralization and vegetative demand. However, these chemical and biological impacts may be overshadowed by physical effects. The relatively high dependency of changes in SO_4^{2-} and SBC on changes in precipitation demonstrates that dilution and variations in drainage are key processes in determining the future chemical properties of streams. The complex and consequential interactions presented here confirm that including the effects of climate change is essential in considering of the future acid-base status of watersheds in the region.

Although CALK is projected to decline by 6.36 µeq L^{-1} by the end of the 21st century under static climate conditions, stream alkalinity would be much lower if not for the implementation of the CAAA. A model run holding deposition of sulfur and all chemical constituents at peak levels from the 1970's and assuming no climate change resulted in loss of CALK of even more (22.2 µeq L^{-1}) by the end of the century (Figure 7). Comparatively, with the input reductions in sulfur deposition and under the MRI-CGCM3 A1fi climate application, stream CALK declines by 12.55 µeq L^{-1}, thereby offsetting the gains offered by the implementation of the CAAA by 39%. This represents a considerable setback to the improvements in stream water quality intended by the CAAA.

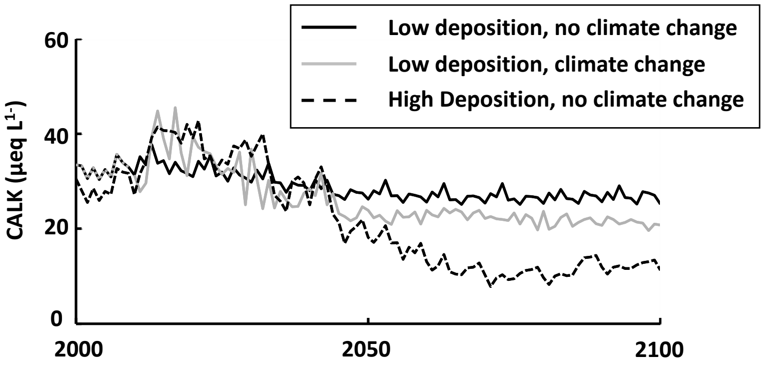

Figure 7: Projections for CALK at WOR1 for the period 2000-2100 under varying deposition and climate scenarios. The MRI-CGCM3 A1fi climate scenario was utilized for the climate change application.

A previous application of PnET-BGC to the Hubbard Brook watershed (HB) (Pourmokhtarian et al., 2012) provides an opportunity to compare the projected effects of climate change on watershed acid-base chemistry in the southern Appalachians versus the northeast. Projections of SO_4^{2-} and base cation concentrations for these two systems are similar, while NO_3^- is quite different. The similarities between the two sites suggest the effects of climate change on variation in SO_4^{2-} and SBC are more pervasive than local. In contrast, little change in NO_3^- is expected at WOR1, whereas 50- to 100-fold increases are predicted at HB. This difference is most likely a result of differing limits on nitrogen demand in the two watersheds and the NO_3^- removal process added in this application. It is important to note that the scope of the study HB and the one presented here differ. The HB investigation focused on CO_2 fertilization effects on forests and future acid-base chemistry, while the study presented here focuses more on isolating the impacts of projected climate change scenarios on the chemical future of acidification and recovery.

Although the decline in stream SO_4^{2-} may signal a positive trend in stream chemistry at WOR1, the overall decline in CALK indicates that the threat of acidification remains, whether a result of episodic events (Wigington et al. 1996), natural disturbances like the gypsy moth defoliation (Webb et al., 1995), or further acidic anthropogenic deposition (Clow et al., 1996). Furthermore, the steep decline in concentration of SO_4^{2-} and SBC signals a dilution of streamwater (Likens and Buso, 2012). Dilution and ion depletion pose concerns to aquatic biota and the watershed ecosystem regardless of acid-base status. For example, calcium depletion has negative consequences ranging from damaging fish health (Rodgers, 1984) to increasing algal blooms (Korosi et al., 2011). Additionally, extremely dilute waters can be harmful to trout development (Enge and Kroglund, 2011) or even human health (Kozisek, 2004). Finally, direct impacts of climate change on the watershed, which include warming waters and an altered hydrologic cycle, present their own complications, ranging from thermally limiting suitable habitat (Flebbe et al., 2006; Durance and Ormerod, 2007) to altering flood and drought patterns (Gasith and Resh, 1999; Lake, 2003).

5.4 Limitation to Modelling Approach

As with any model application, the opportunity exists to improve the efficiency of PnET-BGC in representing WOR1. Foremost, the model application presented here within does not account for vegetative change or disturbance likely from strong climate impacts. Either of these alterations could have significant implications for stream chemistry, possibly exceeding the changes projected to result from climate change itself. For example, the magnitude of change in stream chemical concentrations following the gypsy moth defoliation event in 1989 is comparable to those projected for SO_4^{2-} and SBC and much greater for NO_3^- compared to those projected to occur over the next century (Figure 3). With climate change expected to alter the frequency and intensity of forest disturbance (Dale et al., 2001), the prospect of disturbance remains a concern.

Also of note in PnET-BGC is the routine controlling sulfur cycling. First, the rate of change in SO_4^{2-} concentration appears rather rapid following decline in deposition. In soils with high sulfur adsorption, decreases in stream concentration should be relatively slow as the pool of stored sulfur is predicted to be gradually released into streams over time (Driscoll et al 1998). Though the exact rate of SO_4^{2-} decline is unknown, rates of change observed over that past 30 years suggest the decrease in concentration will take place over decades rather than years (Webb et al., 2004; Sullivan et al., 2007; Robison et al., 2013). Although the Langumuir isotherm added to the SO_4^{2-} adsorption routine in this investigation aided in allowing for greater adsorptions to be achieved in model applications, the predicted change in the stored pool may be faster than what will occur in reality. Geochemical limits on this rate of change need to be included to more accurately model sulfur dynamics, including the irreversibility of some portion of adsorption (Harrison et al., 1989).

Furthermore, for all stream chemical constituents, seasonal patterns of growth and dormancy for vegetation were found to have too large an effect on stream concentration. At3WOR1, seasonal variations in the hydrologic flowpath exert much greater influence on observed streamwater chemical cycles than vegetative demand (Rice and Bricker, 1995), an effect not taken into account by this version of the model. Although the seasonality of stream concentration was not investigated in the present study, which focused on annual averages, improved performance at sub-annual timescales would provide additional confidence in the long-term projections.

6. Conclusion

The impacts of climate change on forested watersheds extend beyond alterations of climate. At WOR1, where acid deposition has been the dominant biogeochemical process for the past few decades, the effect of climate change on acid-base chemistry will likely have serious biogeochemical and ecological implications. This application of PnET-BGC at WOR1 suggests projected changes in climate will most likely impede chemical recovery from acidification. The magnitude of change in variables such as stream discharge, plant growth, decomposition, and evapotranspiration are dependent on the exact climate considered. The particular relationship between individual constituents of stream acid-base chemistry (e.g. SO_4^{2-} or SBC) and these variables results in a complex outlook for WOR1.

Moving forward, additional applications of PnET-BGC to other watersheds in the region are needed to understand if the predicted outcomes are widespread or limited to only WOR1. This is especially meaningful in the southern Appalachians, where bedrock has a substantial influence on biogeochemical watershed characteristics such as base cation supply and SO_4^{2-} adsorption (Robison et al., 2013, Webb et al., 2004). Furthermore, investigations at finer temporal resolutions could reveal changes in seasonality of stream discharge, which could alter the seasonality of element transport and stream chemistry (Likens and Bormann, 1995; Rice and Bricker, 1995). However, this type of investigation is restricted by the model limitations described earlier.

The predicted decline in CALK weakens the intent of federal legislation, specifically the CAAA, which was designed in part to aid in watershed recovery from acidification. The modeled acidification that results from climate change works in opposition of the efforts to limit emissions of SO_2 and NO_x. Nonetheless, the decline in acid deposition already realized as a result of the CAAA has made decreases in stream SO_4^{2-} very likely, limiting alkalinity loss. It is important to remember that the future scenarios predicted here are dependent on input parameters. In the case of acid deposition, if actual declines in SO_4^{2-} and NO_3^- deposition are greater than what is estimated here, it could be enough to curb the decline the CALK caused through climate change. Regardless, if this analysis of WOR1 is representative of the larger population of base-poor watersheds in the southern Appalachians, the outlook for recovery from acidification remains bleak.

7. Acknowledgements

Support for this study was provided by the U.S. Environmental Protection Agency, the National Park Service, the USDA Forest Service, the Virginia Department of Game and Inland Fisheries, Trout Unlimited, the Appalachian Stewardship Foundation, NSF grant EAR-0645697, and the University of Virginia. This paper has not been subjected to agency review and no official endorsement by any agency should be inferred. This paper is a contribution to the Shenandoah Watershed Study. We thank Jack Cosby, James Galloway, Suzanne Maben, and Rick Webb for their input and help throughout this investigation. We would also like to thank

Afshin Pourmokhtarian and Charles Driscoll for their help with learning the intricacies PnET-BGC.

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Chapter 4: Summary and prospects for future research

1. Summary and implications

1.1 Acidification and recovery

Trends in acid anions, base cations, and indicators of acid-base status were investigated at 64 watersheds in the upland watersheds of western Virginia over a 25-year period to examine the current status of acidification and recovery and geochemical controls on those states and trends there within. While pH has increased at a majority of sites across all bedrock types, observed declines in acid neutralizing capacity (ANC) at most sites underlain by base-poor bedrock suggests episodic acidification remains a serious threat to these streams. High sulfate (SO_4^{2-}) adsorption in some watersheds soils constrained significant changes in acid-base chemistry, while the limited supply of base cations at base-poor watersheds led to the general declines in ANC. This work demonstrates that while the relatively small increases in pH indicate an improved chronic acid-base status, the declines in ANC at base-poor watersheds indicate that acidification remains a serious concern for these systems. This study also indicates for the first time that improvements in acid-base chemistry, at least with respect to SO_4^{2-} concentrations, may occur in the near future for-base-poor watersheds in the region.

1.2 Influence of climate change on acid-base chemistry

The potential influence of climate change on future watershed acid-base chemistry was investigated at the White Oak Run (WOR1) watershed in Shenandoah National Park, VA using the biogeochemical model PnET-BGC and statistically downscaled climate scenarios. Although the concentration of SO_4^{2-} was projected to decline regardless of climate scenario utilized, SBC was predicted to decrease even more, leading to a loss of stream alkalinity on average. Both changes in temperature and precipitation were found to have complex effects on these chemical constituents. However, the increased vegetative demand under a warmer climate for base cations is predicted to offset some of the gains in stream alkalinity resulting from reduced acid deposition. This work confirms that climate change will have wide ranging effects on watershed chemistry at WOR1, and will interact with the acid-base chemistry in diverse ways.

2. Avenues of future research

The research presented here demonstrates that the study of watershed acidification and recovery is incomplete. Continued monitoring and analysis is critical in furthering our understanding of how the future of these systems will develop. For example, the potential for depletion of the soil pool of sulfur at WOR1 in the near future represents an important precursor to more generalized recovery. However, the extension of this trend into other watersheds is limited because of the difference in biogeochemical controls and responses across bedrock types. Performing this analysis of the mass balance of sulfur at other watersheds in the region would allow for the investigation of controls on this important process and more precisely determine if and when reduced acidic deposition will have widespread benefits in the region. Furthermore, applying this analysis to other chemical constituents, namely base cations, could reveal interesting and important trends in soil storage. For example, if the soil pool of base cations is increasing, this would indicate soils would be recovering from depletion. Considering that the major driver of base cation loss over the recent past has been acidification, buildup of the soil pool would represent a positive in terms of recovery from acidification. Performing these analyses would further our understanding of biogeochemical controls on ion export from watershed soils and allow for better predictions of the future acid-base status of these systems.

The PnET-BGC model application demonstrates the clear influence of climate change on acidification and recovery at WOR1. When considering how biogeochemical controls vary across watersheds in the region, the extension of this analysis to other watersheds could reveal differing levels of influence of climate change. This would be especially relevant to watersheds underlain by different bedrocks. The Shenandoah Watershed Study (SWAS) program has collected the necessary data for this analysis at three more watersheds, each underlain by different bedrock: Paine Run (siliciclastic), Piney River (mafic and felsic), and Staunton River (felsic). Not only would this provide a more comprehensive examination of the influence of climate change on the prospect of acidification and recovery, it would also further our understanding of the biogeochemical differences between these watersheds.