

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

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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 southern 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 pattern 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.

Keywords Stream acidification · Acid deposition · Acid neutralizing capacity · Base cations · Sulfate adsorption

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 southern Appalachian Mountains. Previous studies in this region have reported little to no

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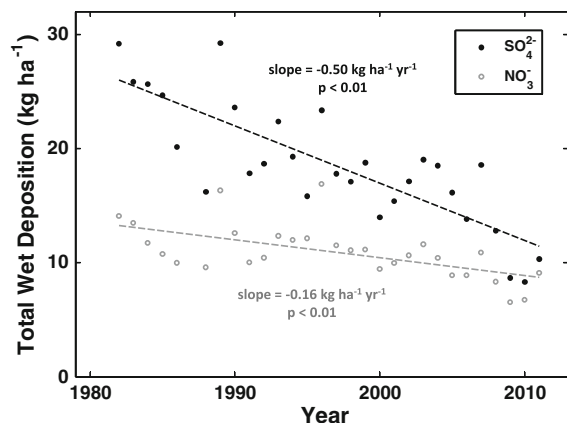


Fig. 1 Time series showing the significant decrease in wet deposition of SO_4^{2-} and NO_3^- at Big Meadows (VA28) in Shenandoah National Park, VA (NADP 2012)

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; Fig. 1) (Webb et al. 2004; NADP (NRSP-3) 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 Appalachian Mountains in western Virginia.

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 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 $50 \mu\text{eq L}^{-1}$ 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 et al. 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, 2004). 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 et al. 2006). However, long-term exposure to acidic deposition depletes base cations from soils, limiting the export to surface waters (Fernandez et al. 2003).

The 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. 2004). 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

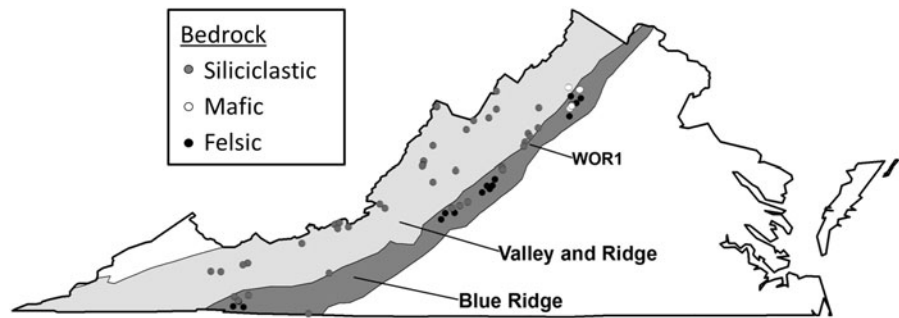
analyses (Webb et al. 2004; Skjelkvåle et al. 2005). Analysis of stream chemistry must therefore include considerations of watershed soils. This is most obvious in the case of SO_4^{2-} , where soil SAC significantly limits the amount⁻ reaching streams. Furthermore, with the large pool of stored SO_4^{2-} 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.

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 to 2011 and in the context of a more detailed weekly time series collected at White Oak Run (WOR1) from 1979 to 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

Fig. 2 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



also has implications for researchers and policymakers in assessing the continued effectiveness of the Clean Air Act and associated amendments.

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 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.

Site description

All watersheds included in this study are located in upland portions of the Valley and Ridge or Blue Ridge physiographic provinces of western Virginia (Fig. 2) (Fenneman 1928). Watersheds are typically small to intermediate in size (<20 km²) 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 Department of Forestry 2005).

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 thought to be susceptible to acidification (i.e. siliciclastic).

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, SO₄²⁻, 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 SO₄²⁻ (EPA Method 300.1; U.S. EPA 1997) and cations (ASTM Method D 6919-03; ASTM 2003).

Table 1 Significance associated with the methods change and subsequent correction factors to align data collected using old instrumentation to the newer instrumentation

Analyte	Median		<i>p</i> value of <i>t</i> test	Correction factors	
	Old method	New method		Coefficient	Intercept
ANC ($\mu\text{eq L}^{-1}$)	34.04	43.15	<0.01	1.01	6.64
pH	6.45	6.32	<0.01	0.96	0.16
SO ₄ ²⁻ ($\mu\text{eq L}^{-1}$)	55.54	53.92	0.01	1.03	-2.45
Ca ²⁺ ($\mu\text{eq L}^{-1}$)	92.57	96.95	0.03	1.06	-1.79
Mg ²⁺ ($\mu\text{eq L}^{-1}$)	90.83	93.33	0.06	–	–
K ⁺ ($\mu\text{eq L}^{-1}$)	12.01	11.41	<0.01	1.03	-1.04
Na ⁺ ($\mu\text{eq L}^{-1}$)	28.83	28.77	<0.01	1.00	-0.39

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

The upgrade and replacement of instrumentation in 2005–2006 created statistically significant, albeit small, changes in all analyte measurements except Mg²⁺ 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.

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 et al. 2004), while utilizing all weekly measurements of SO₄²⁻ in the period of record and daily discharge estimates. Total sulfur storage was calculated for each year of record and is reported in kg S ha⁻¹.

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 (Fig. 3a). Meanwhile, in terms of pH, 64 % of streams displayed a positive trend (Fig. 3b), with each bedrock class displaying a significantly positive median trend of +0.010 pH units year⁻¹ or less. The distribution of trends in ANC is clearly influenced by the dominant bedrock of a particular watershed.

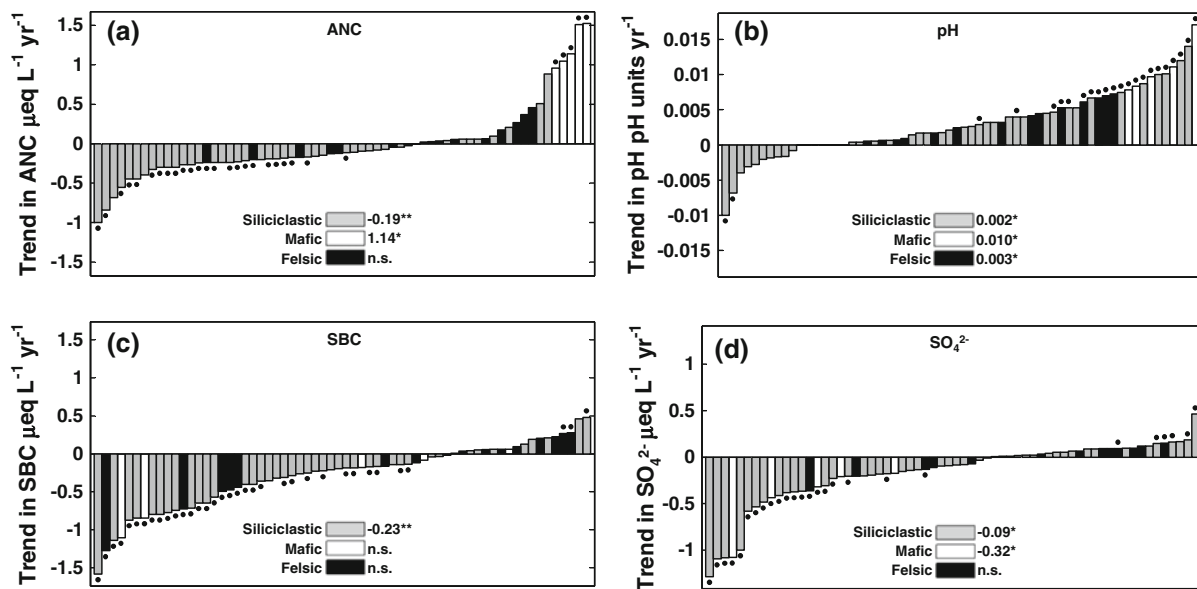


Fig. 3 Bar charts displaying ranked trends of all 64 quarterly sampled sites for **a** ANC, **b** pH, **c** SBC, and **d** SO_4^{2-} (1987–2011). Significance of an individual trend at a 95 % confidence level is indicated by a dot (\cdot). Median trends for each

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

Acidification, classified by a negative trend in ANC, was associated primarily with the base-poor siliciclastic sites (median = $-0.19 \mu\text{eq L}^{-1} \text{year}^{-1}$). All mafic sites exhibited a positive trend in ANC (median = $+1.14 \mu\text{eq L}^{-1} \text{year}^{-1}$), 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 = $-0.23 \mu\text{eq L}^{-1} \text{yr}^{-1}$) was significantly so in this direction (Fig. 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 (Fig. 3d), with significantly negative median values of -0.32 and $-0.09 \mu\text{eq L}^{-1} \text{year}^{-1}$ respectively.

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 (Fig. 4).

Of those watersheds with increasing ANC (Fig. 4a, 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 (Fig. 4c, 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.

The average initial concentration of SBC, defined as the average concentration over the first 2 years of monitoring, positively relates with the trend in ANC (Fig. 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 = $342 \mu\text{eq L}^{-1}$) than either felsic ($146 \mu\text{eq L}^{-1}$) or siliciclastic ($133 \mu\text{eq L}^{-1}$) sites,

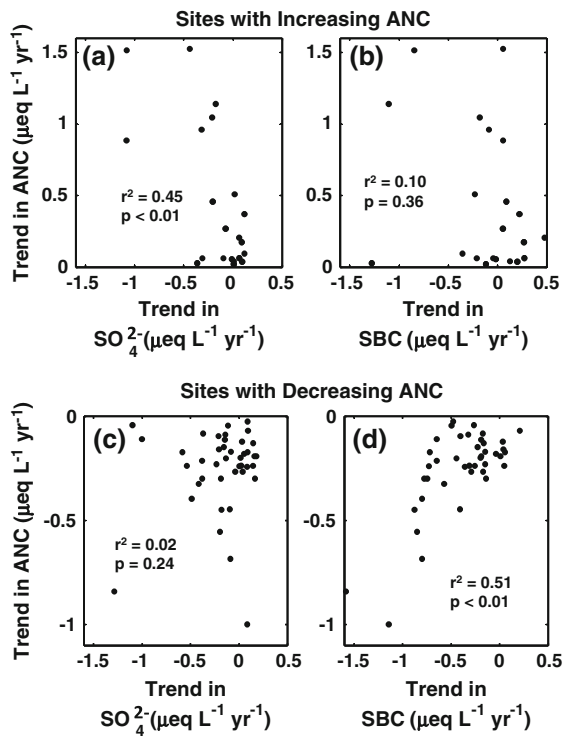
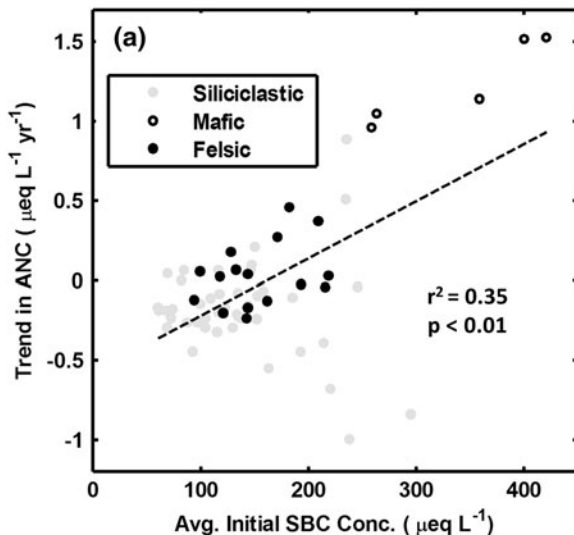


Fig. 4 Linear regression of the trends in ANC versus the trends in SO_4^{2-} and SBC separated for sites that show increasing ANC (a and b) over the time period and sites that show decreasing ANC (c and d)



demonstrating the greater base cation supply of watersheds underlain by mafic bedrock.

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 (Fig. 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 $36.2 \mu\text{eq L}^{-1}$, which is nearly half that of both mafic ($57.1 \mu\text{eq L}^{-1}$) and siliciclastic ($63.5 \mu\text{eq L}^{-1}$) sites.

Discussion

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

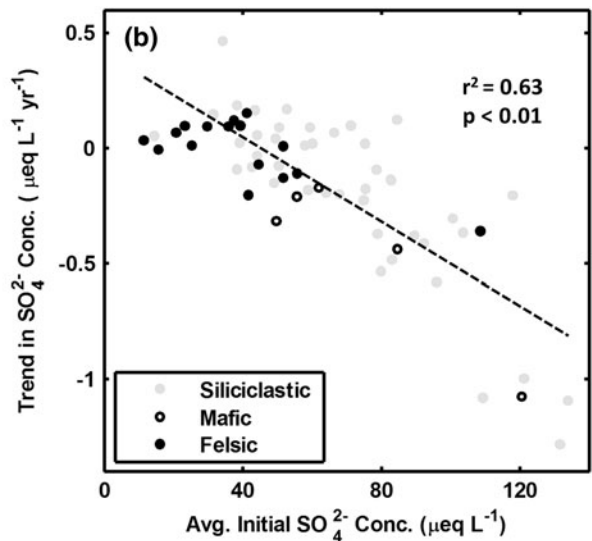


Fig. 5 Regression of (a) the trends in ANC versus the average initial SBC concentration and (b) the trends in SO_4^{2-} versus the average initial SO_4^{2-} concentration for all 64 sites. Note the clear

distinction between bedrock classes and the initial condition for both SBC (mafic markedly greater) and SO_4^{2-} (felsic markedly lower)

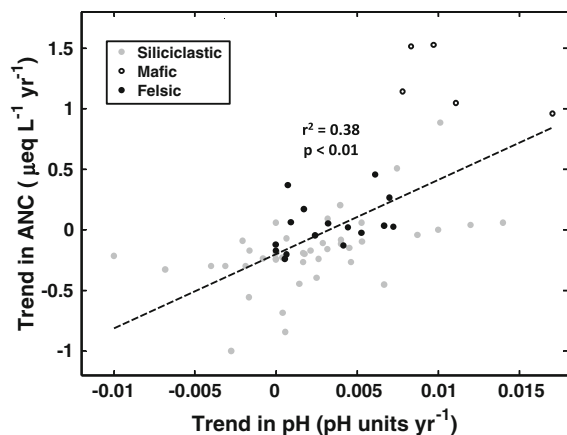


Fig. 6 Regression of the trends in ANC versus the trends in pH for all 64 sites. The significant positive relationship is consistent with the theoretical relationship between these two variables

for most watershed studies in this region (Webb et al. 2004; Skjelkvåle et al. 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.

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 (Monteith 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 ($r^2 = 0.38$, $p < 0.01$; Fig. 6).

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 in pH is 0.41 units, and 86 % of sites had a calculated total increase of <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 stream-water 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.

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 (Fig. 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 pattern 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 (Fig. 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.

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 (Fig. 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 2 years. Also of note, net sulfur storage has decreased at a rate of

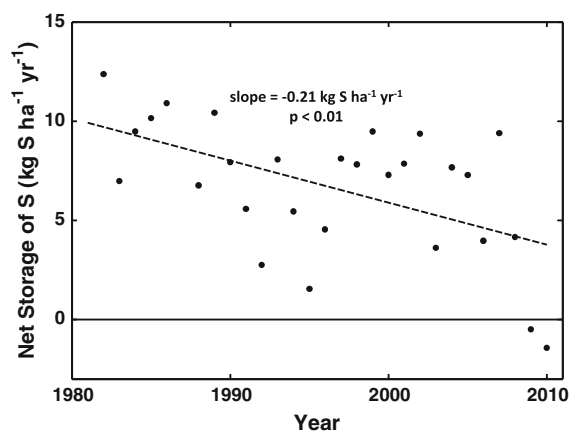


Fig. 7 Mass balance analysis of sulfur at WOR1. The calculated total storage is shown for each year of record and the linear regression line is plotted through the data to show the significant decreasing trend

$-0.21 \text{ kg S ha}^{-1} \text{ year}^{-1}$ ($p < 0.01$) 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.

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.

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.

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