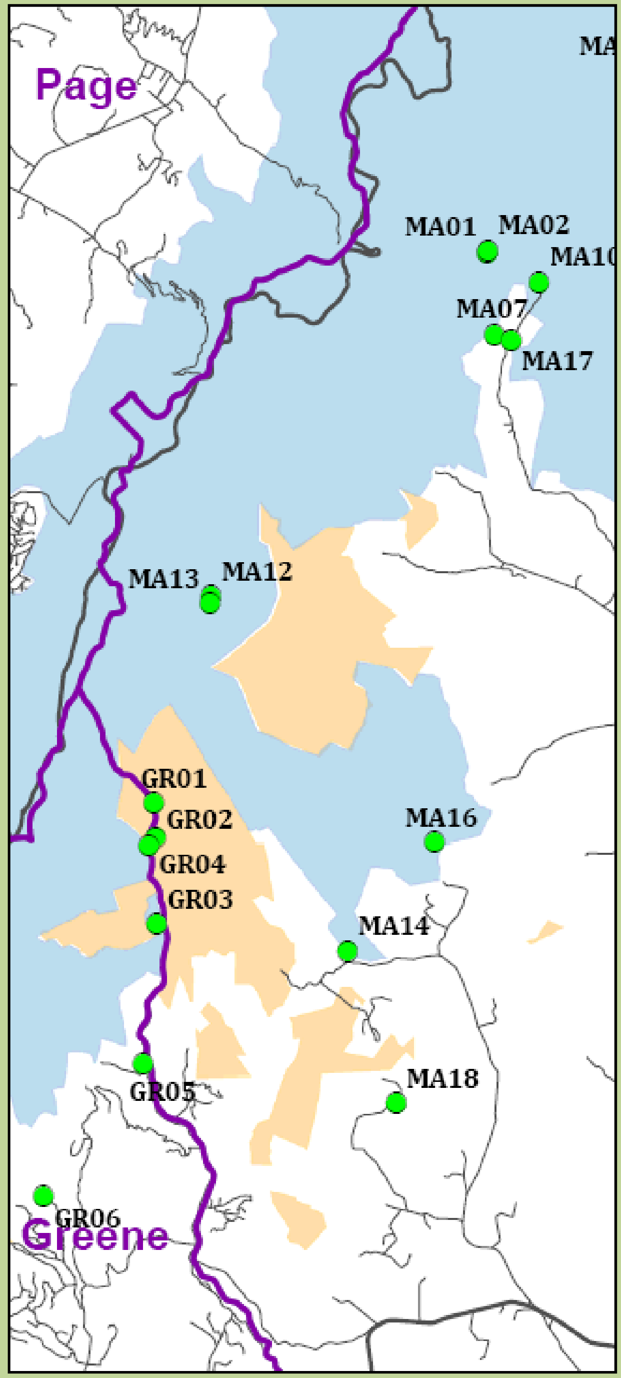
Virginia Trout Stream Sensitivity Study
2010 Survey
Results for Shenandoah National Park



Virginia Trout Stream Sensitivity Study
2010 Survey

Results for Shenandoah National Park

prepared by

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1.0 INTRODUCTION

The Virginia Trout Stream Sensitivity Study (VTSSS) is designed to track the effects of acidic deposition and other factors that determine water quality and related ecological conditions in Virginia's native trout streams. The VTSSS 2010 survey was the third regional survey conducted with the assistance of Trout Unlimited and other volunteer organizations. Previous surveys were conducted in 1987 and 2000. The VTSSS 2010 survey established a decadal time-frame for regional surveys that ideally will be maintained going forward.

Following the first VTSSS regional survey in 1987, a geographically distributed subset of streams was selected for long-term monitoring. This component of VTSSS now includes 67 streams in the mountainous region of western Virginia that are sampled on a seasonal (quarterly) basis.

The VTSSS program is coordinated and managed in conjunction with the Shenandoah Watershed Study (SWAS), a long-term research and monitoring program focused on Shenandoah National Park (SHEN). The SWAS program was begun in 1979 as a cooperative undertaking of the Department of Environmental Sciences at the University of Virginia (UVA) and natural resource managers at SHEN. Stream water monitoring associated with the SWAS program includes sampling and data collection conducted at multiple spatial and temporal scales. Weekly grab sampling is conducted at six sites (This number was reduced to four in 2011). Three of the weekly sampling sites are also sampled at higher frequency with automated samplers during episodic high-discharge conditions. Continuous discharge gauging is maintained at three of the six weekly sampling sites. Coordination with the VTSSS program provides additional seasonal (quarterly) sampling at 14 sites in SHEN, as well as the more-synoptic sampling conducted in SHEN as part of the VTSSS regional surveys.

The long-term data provided through the combined SWAS-VTSSS programs have proven important to both local resource management and to the development, evaluation, and implementation of national air pollution control policies. Information provided through these programs has served to identify the central Appalachian Mountain region, including western Virginia and SHEN, as among the areas of the U.S. that are most susceptible to the effects of acidic deposition, most subject to continuing acidification of surface waters, and most resistant to recovery following reduced atmospheric emissions and deposition of acidic pollutants (Stoddard et al., 2003, Sullivan et al., 2004; Cosby et al., 2006).

The data obtained through the VTSSS 2010 survey have provided an opportunity to assess changes in the acid-base status of streams in western Virginia. This report focuses, in particular, on the subset of VTSSS 2010 survey sites in SHEN and on three water quality parameters that are key to assessment of change in the acid-base status of streams: acid neutralizing capacity (ANC), sulfate, and the sum of base cations.

2.0 SURVEY DESIGN AND METHODS

The VTSSS program tracks changes in the chemical properties of streams that drain the forested mountains of western Virginia and support reproducing populations of the native brook trout (*Salvelinus fontinalis*). Selection of streams for the initial regional survey in 1987 was based on records of native brook trout distribution maintained by the Virginia Department of Game and Inland Fisheries. Sampling sites for the initial 1987 survey were selected to obtain the maximum number of independent sites meeting general watershed size and disturbance criteria. The minimum size of watersheds included in the survey was established as those for which the distance from the sampling site to the most distant point in the watershed above the sampling site was at least one mile. Candidate sites were further screened to avoid streams with extensive direct anthropogenic disturbance in the watersheds above the sites (e.g. roads, agriculture, residential development). In addition, some streams associated with limestone bedrock (therefore highly alkaline) were not included. Other streams were not included due to access problems. In all, about 80% of Virginia's native brook trout streams were sampled in the initial 1987 survey.

Sample collection sites in the 2000 and 2010 surveys included most of the sites sampled in 1987. A number of sites established as quarterly sampling or seasonal sampling sites were added to the list of sites included in the surveys. The total numbers of sites sampled in the 1987, 2000, and 2010 surveys were, 394, 452, and 458, respectively. These numbers include designated weekly and quarterly sampling sites that, along with the survey sites, were sampled during survey sampling windows. Figure 1 indicates the locations of survey, quarterly, and weekly sites sampled in the 2010 survey.

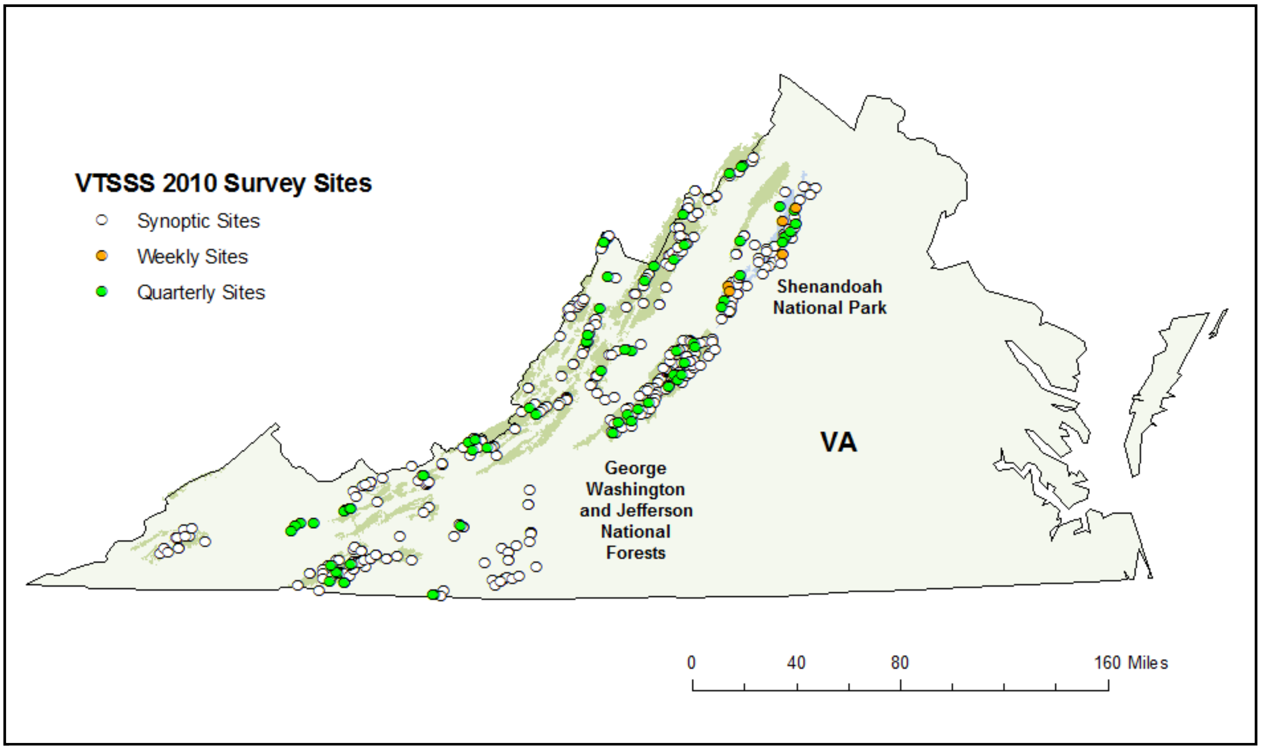


FIGURE 1 - Distribution of stream sites sampled during the VTSSS 2010 sample collection window (N = 456).

The primary sampling windows for the three regional surveys was defined as the last seven days in April for each of the survey years. For sites for which no sample was collected in the primary window, the sampling window was incrementally expanded to 21 days, including seven days before and after the primary window. A springtime sampling window was chosen to obtain samples representing the period of the year in which streams typically have the lowest acid neutralizing capacity (ANC).

Sample collection for each of the surveys was organized as a collaborative effort with the Virginia Council of Trout Unlimited. Information concerning the VTSSS 2010 survey sample collection is posted at http://swas.evsc.virginia.edu/VTSSS-2010/Survey.html. This website provides an overview of the 2010 survey, including instructions for sample collectors, sample collection forms, and county maps indicating sample locations. Sample collectors were also provided with detailed site documentation, including maps and site photographs. The VTSSS

2010 survey effort involved 21 regional sample collection coordinators and 165 sample collectors. The previous surveys involved similar numbers of coordinators and volunteers.

Sample handling and analysis conformed with methods described in Webb et al. (2010). Analyses included pH, ANC, specific conductivity, sulfate, nitrate, chloride, calcium ion, magnesium ion, potassium ion, sodium ion, and silica. Data and metadata, including site documentation, for the three surveys is maintained in a SWAS-VTSSS program installation of NPSTORET, a relational database developed by the National Park Service. Data and metadata for the three surveys has been submitted to the National Park Service in NPSTORET format, as well as in Microsoft ACCESS and Excel formats that do not require access via NPSTORET.

Appendix 1 of this report lists VTSSS 2010 survey data for SHEN, including stream water analysis and sample site location data. The records are provided in Excel format and ordered from lowest-to-highest acid neutralizing capacity (ANC). As described below, most of the sites are within the park boundary; a small number are adjacent the park on streams that flow out of the park.

3.0 VTSSS 2010 REGIONAL SURVEY CONTEXT

3.1 Comparison Between Regional Surveys

Miller (2011) examined data obtained through the 1987, 2000, and 2010 regional surveys as a basis for assessing the long-term response of water chemistry in Virginia's mountain streams to decreases in atmospheric acidic deposition that resulted from emissions reductions. For this study, evidence for recovery was identified by a decrease in stream water concentrations of sulfate and an increase in stream water ANC. Consistent with general recovery, the analysis showed that between 1987 and 2010, median stream sulfate concentrations declined 18% (12.9 μeq/L) and median stream ANC increased 76% (44.4 μeq/L). Miller (2011) also analyzed a number of spatial, geographic, and geological characteristics to identify factors responsible for variation in stream recovery from acidification. The results of this analysis included the following:

- Bedrock geology was correlated with the magnitude of concentrations of ANC and sulfate but was not related to rates of change in the concentrations of ANC and sulfate.

- Sample site elevation exhibited a weak but significant association with the rate of recovery from acidification, with lower elevation sites showing slightly more recovery between surveys.
- There was no relationship between watershed area and stream recovery from acidification.
- The gypsy moth defoliation of the 1990s did not appear to affect recovery from acidification.
- Differences in weather or hydrologic conditions did not appear to affect the observed pattern in stream recovery from acidification.
- Spatial variability in atmospheric sulfate deposition may be an important factor in the spatial distribution of recovery.

Miller (2011) further observed that streams in the mountains of Virginia may have reached a turning point with respect to acidification and recovery. Whereas surface waters in the northern Appalachian region of the country showed substantial signs of recovery in the decade immediately following enactment of the Clean Air Act Amendments of 1990, streams in the mountains of Virginia have shown a more lagged response, a pattern attributed to greater sulfate adsorption in watershed soils. The substantial improvement indicated by the VTSSS 2010 survey data suggests that recovery, although delayed, is now occurring in Virginia mountain streams. Miller (2011), however, qualifies this assessment by noting that future data collection will reveal whether streams in the Virginia mountains are responding to reduced acidic deposition or if these streams appear less acidic for other reasons.

3.2 Results in SHEN Compared to the Larger Study Region

As indicated above, the total number of stream sites sampled during the VTSSS 2010 survey window was 458. Of these, 14 streams were treated with limestone to neutralize acidity at some point during the 23 years between 1987 and 2010 surveys. The data for these 14 streams are not included in the analysis provided in this report. Another two sites are not included in the analysis due to upstream disturbance. Of the 442 stream sites remaining in the VTSSS 2010 data set, 66 stream sites were located within SHEN or on streams that flow out of SHEN within 1.6 km of the SHEN boundary and upstream of evident disturbance (e.g., cleared land, buildings, impoundments). Figure 2 indicates the location of the 66 streams associated with SHEN.

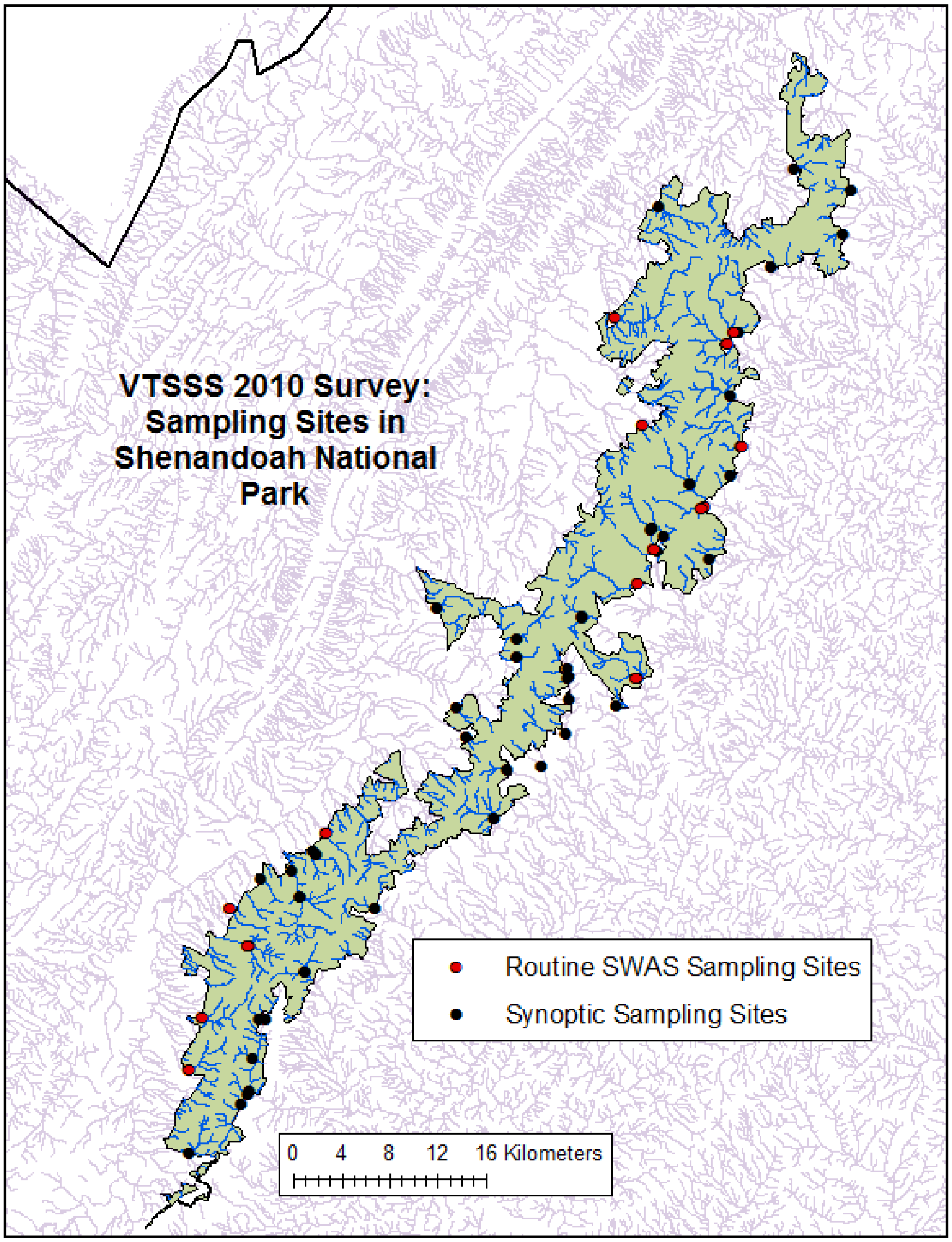


FIGURE 2 - Distribution of stream sites sampled in or adjacent SHEN during the VTSSS 2010 sample collection window (N = 66). Of these, 52 are synoptic sites and 14 are routine sampling sites (eight quarterly and six weekly).

Table 1 compares median stream water ANC, sulfate, and sum of base cation concentration values for the VTSSS 2010 survey sites in SHEN (n = 66) and the other sites in the broader VTSSS 2010 survey region (n = 376). Figure 3 compares the interquartile distribution and range of ANC, sulfate, and sum of base cation concentration values for the SHEN survey sites and the other regional survey sites.

TABLE 1 - Comparison of median values for VTSSS 2010 survey samples collected in or adjacent SHEN and samples collected elsewhere in the western Virginia survey region.

	SHEN (n = 66)	Western VA (n = 376)	p value[1]
ANC (μeq/L)	124.5	93.6	0.023
Sulfate (μeq/L)	66.4	58.9	0.142
Sum of base cations[2] (μeq/L)	219.9	186.9	0.083

[1] The Independent Samples Median Test (SPSS, 2011) was applied to test differences in median values. Null hypothesis: the medians are the same.

[2] The sum of base cations is equal to the sum of calcium ion, magnesium ion, potassium ion, and sodium ion concentrations.

Although the median values for ANC, sulfate, and the sum of base cations are all greater for the SHEN sample sites than for the other sample sites in the broader survey region, only the difference in ANC is statistically different at $p < 0.05$. The higher median ANC values in SHEN are consistent with previously observed differences related to differences in bedrock between the Blue Ridge Mountain and the Ridge and Valley physiographic provinces (Webb et al., 1989). The mafic and felsic lithologies of the Blue Ridge Mountain Province, including SHEN, are generally associated with higher stream water ANC than the siliceous and argillaceous lithologies of the ridges in the Ridge and Valley Province.

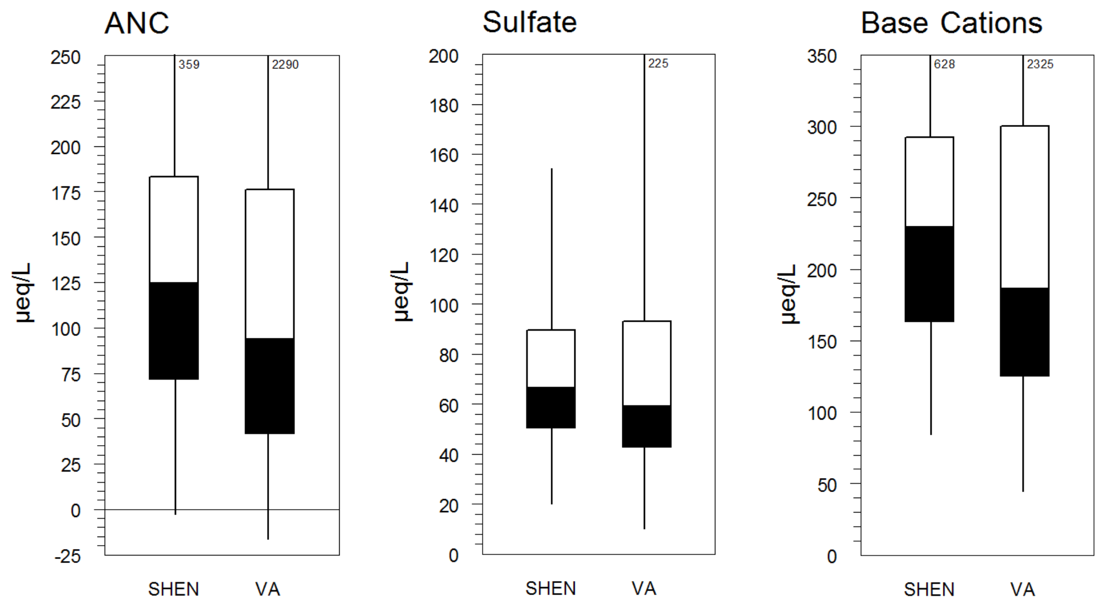
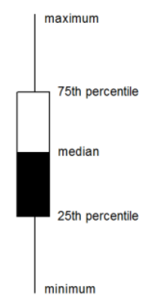


FIGURE 3 - Comparison of median, inter-quartile distribution, and range for ANC, sulfate, and the sum of base cations measured in VTSSS 2010 survey samples collected in Shenandoah National Park (n = 66) and outside of the park in western Virginia (n = 376).



4.0 CHANGE BETWEEN SURVEYS IN SHENANDOAH NATIONAL PARK

4.1 Change in Acid-Base Composition of Stream Water

Of the 66 stream sites sampled in SHEN during the VTSSS 2010 sampling window, 55 sites were also sampled during the 1987 and 2000 surveys. Table 2 lists the median concentrations for ANC, sulfate, and the sum of base cations for the 55 sites sampled in each of the three surveys. Figure 4 compares the interquartile distribution and range of ANC, sulfate, and sum of base cation concentrations for the 55 sites sampled in each of the three surveys. Table 3 lists the medians of the differences in concentrations for ANC, sulfate, and sum of base cations between samples collected at the same sites in each of the three surveys, including comparisons between samples collected in 1987 and 2010 (the entire record), 1987 and 2000 (the first interval), and 2000 and 2010 (the second interval). Figure 5 compares the interquartile distribution and range of the differences in ANC, sulfate, and sum of base cation concentrations between samples collected at the same sites in each of the three surveys.

TABLE 2 - Median stream water concentrations for stream sites sampled in all three VTSSS surveys (n = 55).

	1987 Survey	2000 Survey	2010 Survey
ANC (µeq/L)	76.0	86.7	121.0
Sulfate (µeq/L)	83.0	78.9	66.5
Sum of base cations (µeq/L)	178.0	195.9	215.5

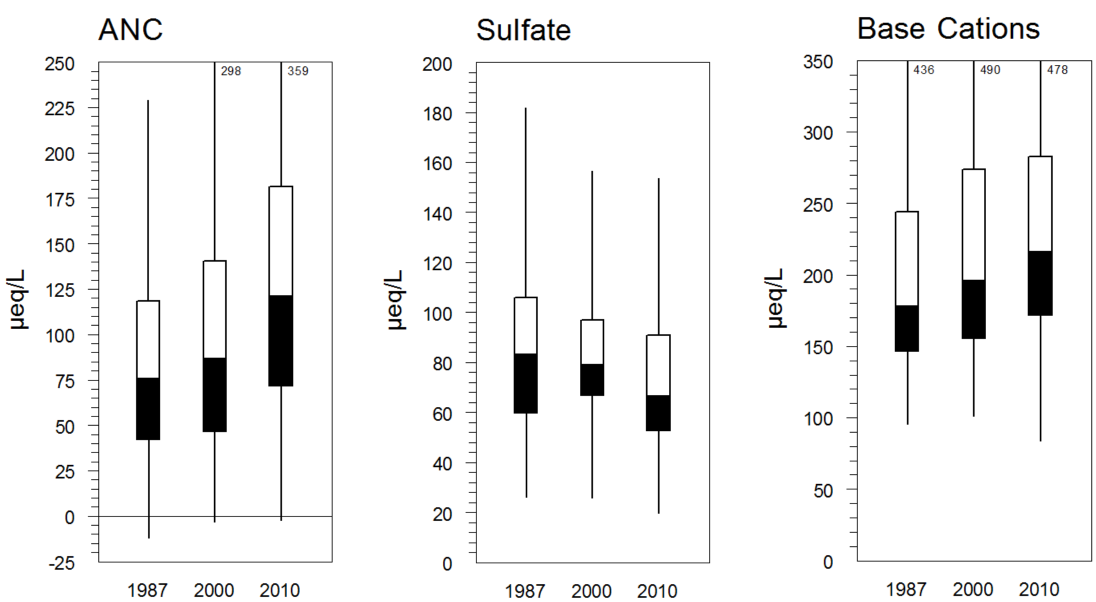


FIGURE 4 - The interquartile distribution and range of ANC, sulfate, and sum of base cation concentrations for the 55 sites sampled in each of the three surveys.

TABLE 3 - Medians of differences in stream water concentrations for samples collected at the same sites in each of the three surveys.

	1987-2010		1987-2000		2000-2010	
	Median[1]	p-value[2]	Median[1]	p-value[2]	Median[1]	p-value[2]
ANC (µeq/L)	+47.7	0.000	+10.0	0.000	+29.6	0.000
Sulfate (µeq/L)	-11.8	0.000	-1.5	0.082	-11.0	0.000
Sum of base cations (µeq/L)	+33.3	0.000	+18.6	0.000	+7.7	0.000

[1] The median of differences between samples collected at the same sites.

[2] The Related-Samples Wilcoxon Signed Rank Test (SPSS, 2011) was applied to test the medians of differences. Null hypothesis: the median of differences equals 0.

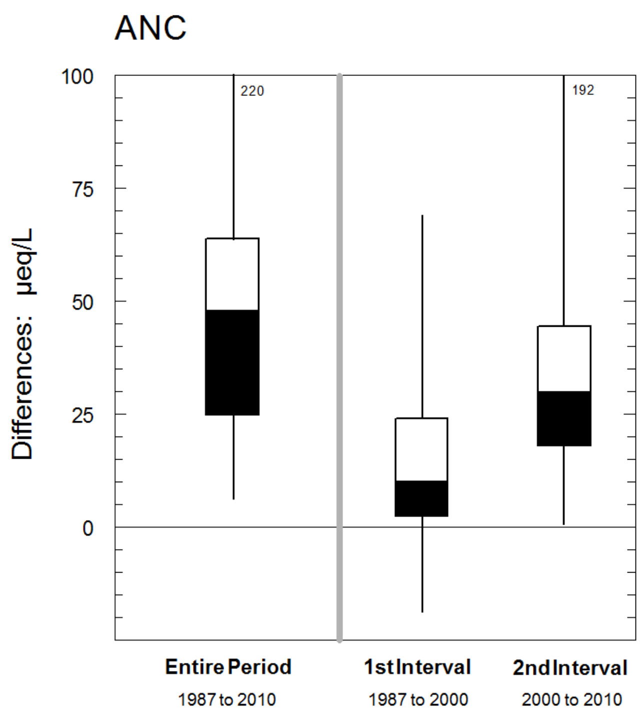
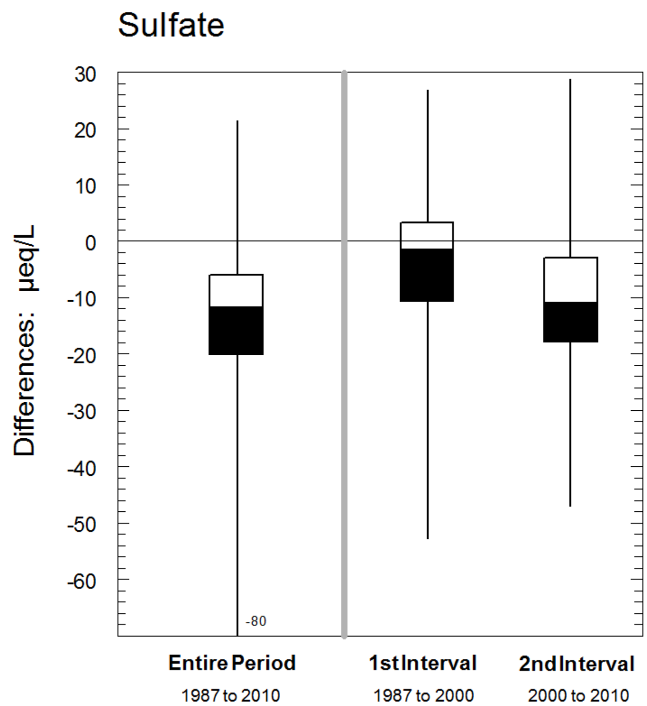


FIGURE 5 - The interquartile distribution and range of the differences in ANC concentrations between samples collected at the same sites in each of the three surveys.



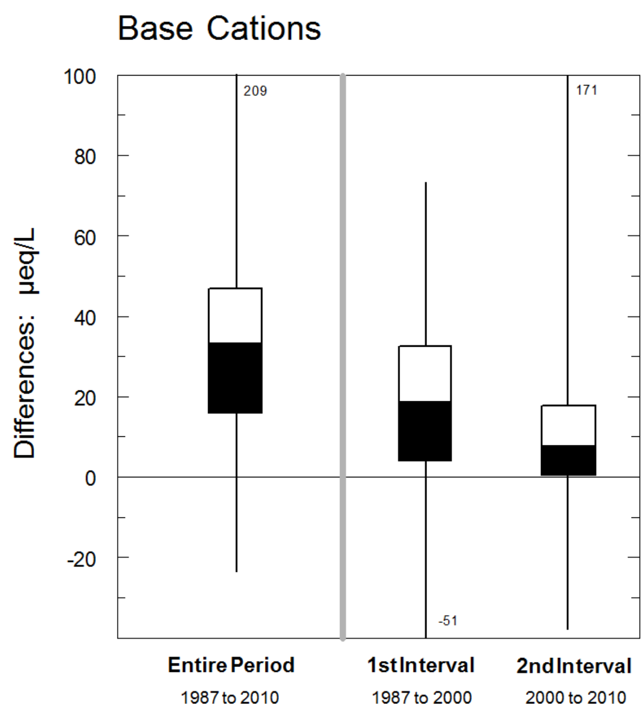


FIGURE 5 *continued* - The interquartile distribution and range of the differences in sulfate and sum of base cation concentrations between samples collected at the same sites in each of the three surveys.

The observed changes in stream water concentrations of ANC, sulfate, and base cations indicate improving water quality in SHEN streams during the 23-year period spanned by the three VTSSS surveys. The pattern of change suggests that the improvement is due to the combined effect of multiple factors.

Increasing concentrations of ANC and decreasing sulfate concentrations are consistent with at least partial recovery from stream water acidification caused by atmospheric acidic deposition. Between 1987 and 2010, the median of stream sulfate concentrations declined 20% (16.5 µeq/L) and the median of stream ANC concentrations increased 59% (45.0 µeq/L). These changes in SHEN are similar to the changes described by Miller (2011) for the larger survey region (see Section 3.1, above).

Between 1987 and 2010, the median of base cation concentrations in SHEN streams increased 21% (31.5 µeq/L). This increase in base cations contributed to the increase in ANC. The increase in median ANC cannot be fully explained by the decrease in median sulfate, which is less than half the increase in median ANC. It is also relevant to the issue of ANC recovery that increasing concentrations of base cations are not commonly associated with reduced acidic deposition and reduced sulfate concentrations in surface waters. The expected and generally observed response to reduced sulfate mobility in watershed systems is a decrease in base cation concentrations in surface waters, which has the effect of limiting or even preventing ANC increase (Galloway et al., 1983; Stoddard et al., 1999; Sullivan et al., 2003). It thus appears that factors other than reduced acidic deposition are responsible for part of the increase in or apparent recovery of ANC in SHEN streams that is indicated by the survey data.

Examination of the two time intervals defined by the three surveys provides additional perspective on the increase in ANC in SHEN streams. Most of the change in ANC occurred in the second interval. The median of differences in ANC between samples collected in the 2000 and 2010 surveys (+29.6 µeq/L) was approximately three times the median of differences between samples collected at the same sites in the 1987 and 2000 surveys (+10.0 µeq/L).

Corresponding to the timing of the increase in ANC, most of the decrease in sulfate concentrations occurred in the second interval. The median of differences in sulfate concentrations between samples collected in the 2000 and 2010 surveys (-11.0 µeq/L) was larger than the median of differences between samples collected at the same sites in the 1987 and

2000 surveys (-1.5 µeq/L and not significantly different than zero). The larger decrease in sulfate concentration in SHEN streams in the second interval, between the second and third surveys, is consistent with the temporal pattern of sulfate deposition measured in SHEN. Deposition during the second time interval was substantially less than during the preceding years.

As indicated in Figure 6, sulfate deposition measured in precipitation at Big Meadows in SHEN during the 2001-2010 decade was less than in the earlier years of the 1982-2010 record. Over the 28-year record period, sulfate deposition declined from above 25 kg/ha/yr to less than 10 kg/ha/yr, with the lowest annual deposition values in the record occurring in the last three years. Also, the annual rate of decrease in deposition increased during the 10 years between the 2000 and 2010 surveys. Whereas the rate of decrease for both the entire precipitation record and the years between the first and second surveys was -0.49 kg/ha/yr, the rate of decrease for the years between the second and third surveys was -0.95 kg/ha/yr.

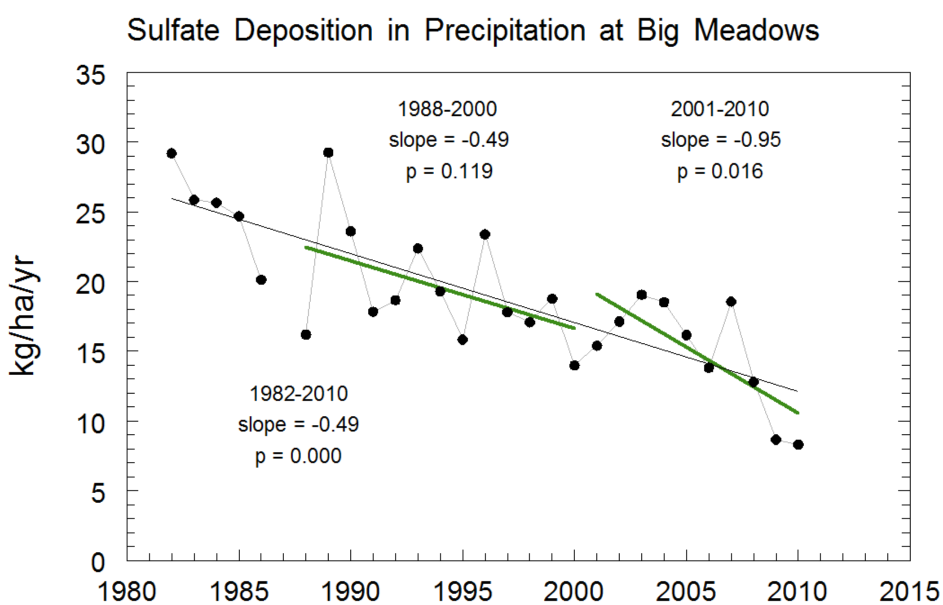


FIGURE 6 - Sulfate deposition measured in precipitation at Big Meadows in Shenandoah National Park. The data were obtained from the National Atmospheric Deposition Program (NADP, 2012). Trends for the entire record and for the time intervals between VTSSS stream surveys were determined by linear regression (SPSS, 2011).

In contrast with the timing of the changes in both ANC and sulfate concentrations, the larger change in base cation concentrations in SHEN streams occurred during the interval between the first two surveys. The median of differences in base cation concentrations between samples collected in the 1987 and 2000 surveys (+18.6 µeq/L) was more than two times the median of differences between samples collected at the same sites in the 2000 and 2010 surveys (+7.7 µeq/L). A number factors can be listed as possible explanations for the increase in base cations, as well as the timing of the increase. Among these are:

- Differences in stream discharge between the three survey windows. Higher discharge in the 1987 survey window could be associated with base cation dilution, resulting in lower concentrations in the first survey and higher concentrations in later surveys.
- Redistribution of base cations due to the gypsy moth infestation. Base cation concentrations in streams transiently increased following defoliation. The increased mobility of base cations may have also increased longer-term base cation availability in the soil exchange complex.
- A change in the mobility of organic anions. The increase in base cations may be associated with unmeasured weak acid anions.
- Increased soil temperature. Higher soil temperature might increase microbial and root respiration, leading to increased base cation mobilization through an increase in carbonic acid weathering or exchange.

Additional research and analysis will be required before the effect and relative importance of these and other possible explanations for the increase in base cation concentrations can be determined.

4.2 Change in Relation to Biological Response Class

Figure 7 indicates the locations of the 55 stream sites in SHEN that were sampled in all three VTSSS surveys. The sites shown are classified based on an ANC value of 50 µeq/L, a value that is commonly adopted as a threshold for biological response to acidification. Bulger et al. (2000), for example, developed ANC categories for brook trout response to acidification in forested headwater catchments in western Virginia. According to this classification, streams with ANC greater than or equal to 50 µeq/L are "not acidic" or are suitable for reproducing brook trout populations where other habitat conditions are also suitable. Streams with ANC less than 50 µeq/L are otherwise classified as "indeterminate" (ANC 20 to < 50 µeq/L), "marginal" (ANC > 0

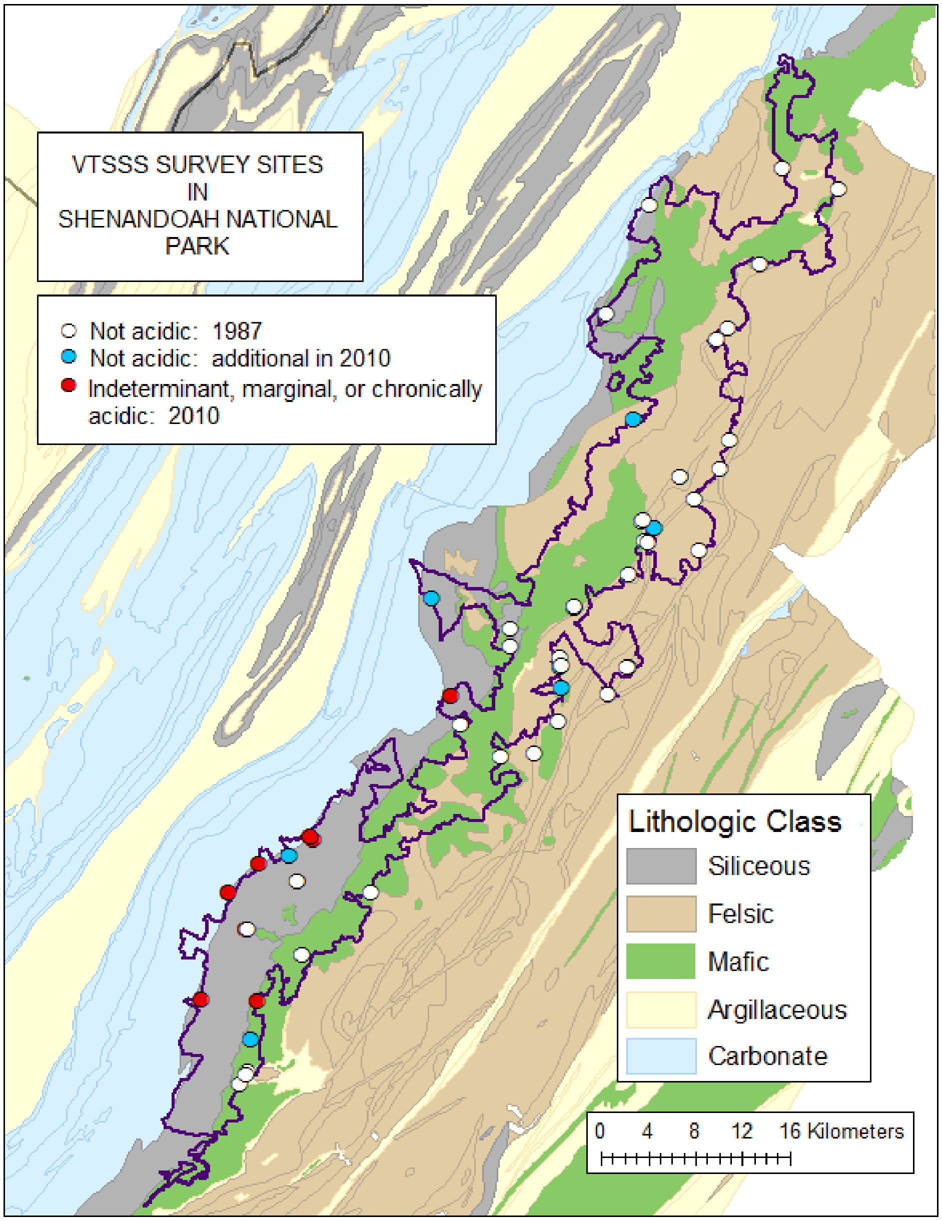


FIGURE 7 - Distribution of VTSSS survey sites in Shenandoah National Park and change in acid-base status between the 1987 and 2010 surveys. The white symbols represent stream sampling sites where ANC was greater than 50 µeq/L in 1987. The blue symbols represent additional sites with ANC greater than 50 µeq/L in 2010. The red symbols represent sites with ANC less than 50 µeq/L in 2010. The map also indicates the distribution of major lithologic classes in the region (based on Sullivan et al, 2007).

to < 20 µeq/L), or "chronically acidic" (ANC < 0 µeq/L). The value of 50 µeq/L has similarly been cited by other investigators as an indicator or reference value for effects of acidification (e.g., USEPA, 2010). It is also notable that modeling conducted by Sullivan et al. (2008) indicates that the ANC of all streams in SHEN, including streams that currently have much lower ANC, exceeded 50 µeq/L prior to the effects of acidic deposition.

As indicated in Figure 7, the number of SHEN streams in the "not acidic" (ANC >50 µeq/L) category increased between the 1987 and 2010 surveys. A number of streams, however, remained in the categories associated with lower ANC. In 1987, the number of streams with ANC < 50 µeq/L was 17, or 34.0% of the total number of streams sampled in both the 1987 and 2010 surveys. In 2010, the number of streams with ANC < 50 µeq/L decreased to 9, or 16.4% of the surveyed streams.

All of the streams with ANC < 50 µeq/L in 2010 drain watersheds that are predominantly (at least 87%) underlain by relatively base-poor siliceous (siliciclastic) bedrock. Dynamic critical loads analysis conducted for SHEN by Sullivan et al. (2008) identified the class of streams associated with base-poor siliceous bedrock as the least responsive to reductions in sulfate deposition. For some of the siliceous streams included in their analysis, there was no level of deposition reduction predicted to achieve ANC > 50 µeq/L by the year 2040. In other words, for a subset of SHEN streams, even immediate reduction of sulfate deposition to zero would not achieve pre-acidification, biologically suitable ANC levels in the time-frame considered. Sullivan et al. (2008) identified depletion of base cations in watershed soils in response to decades of relatively high sulfate deposition as the probable cause for this poor prognosis. They did not, however, expect or account for the increase in base cations concentrations in stream water that is now observed. Without this increase in base cation concentrations the recovery or increase in the number of streams with ANC > 50 µeq/L would be less. Additionally, the current level of recovery may not be sustained if the increase in base cations proves temporary. Moreover, the evident increase in the current export of base cations in stream water may be associated with accelerated depletion of the supply of available base cations in watershed soils, which would diminish the prospect for long-term recovery.

5.0 ASSOCIATIONS BETWEEN CHANGE IN STREAM WATER COMPOSITION AND LANDSCAPE FACTORS

5.1 Watershed Bedrock

Bedrock distribution is associated with a broad range of ecological properties in SHEN. Bedrock differences have been shown to account for much of the variation in soil chemistry (Welsch et al., 2001; Cosby et al., 2006), vegetation (Young et al., 2006), and aquatic biota (Bulger et al., 1999; Cosby et al., 2006). A strong relationship between watershed bedrock and the acid-base chemistry of stream waters, in particular, has been well established (Lynch and Dise, 1985; Bulger et al., 1999). Relative to the major bedrock classes in SHEN, concentrations of ANC and related ions derived from watershed sources decrease in the following order:

mafic (basaltic) > felsic (granitic) > siliceous (siliciclastic)

More recently, Snyder et al. (2011) examined the relationship between bedrock distribution and the composition of small headwaters streams (100 ha watersheds) in SHEN, finding that the general relationship with bedrock class holds, but variation is greater than for larger streams and watersheds due mainly to a disproportionate effect of inaccurate bedrock classification .

Sullivan et al. (2003) examined trends (1988-2001) in acid-base chemistry for quarterly data obtained for the 14 SWAS program study streams in SHEN. They found that the median annual and spring season trends in ANC were positive for all of the lithologically defined subsets of streams, with the largest increases associated with the mafic subset. The median annual and spring season trends in sulfate concentrations were negative for all of the lithologically defined subsets of streams. The median annual and spring season trends in base cation concentrations were negative for the siliceous and felsic subsets, but positive for the mafic subset.

As described in Section 3.1 of this report, Miller (2011) examined bedrock distribution in relation to stream water composition data (ANC and sulfate) obtained through the VTSSS surveys in the entire western Virginia study region, finding an association between the magnitudes of ANC and sulfate concentrations, but no association with rates of change in concentration. The association between bedrock and changes in acid-base chemistry observed for the SHEN subregion are examined here by direct comparison of 1987 and 2010 results (Figure 8), by linear regression (Table 4), and by estimation of mean change associated with the three bedrock types (Figure 9).

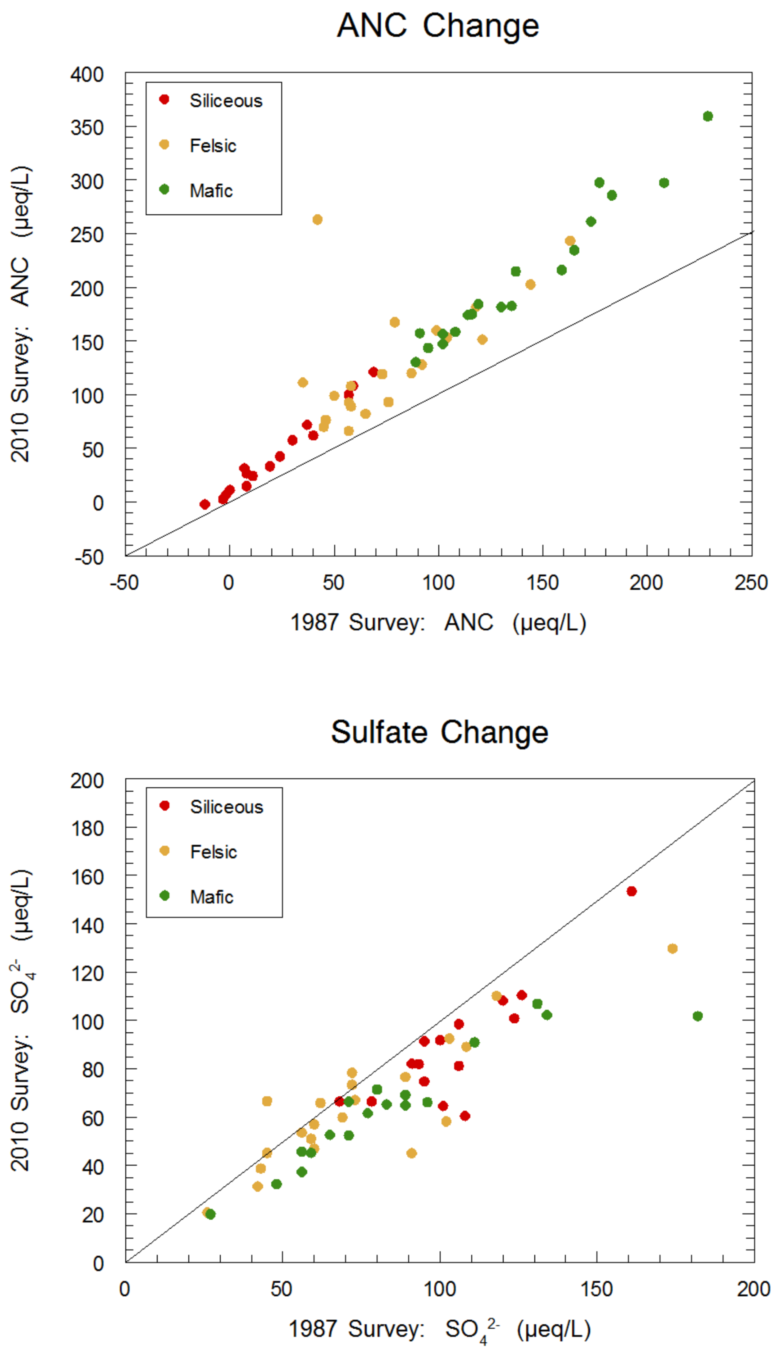


FIGURE 8 - Comparison of 1987 and 2010 VTSSS survey data obtained in Shenandoah National Park (n = 55). Points below the diagonal 1:1 line indicate higher values in 1987; points above the line indicate higher values in 2010. Points are coded by dominant watershed bedrock class based on watershed area > 50%. Some points are thus associated with multiple bedrock classes. Watershed bedrock classification is based on (Sullivan et al., 2007).

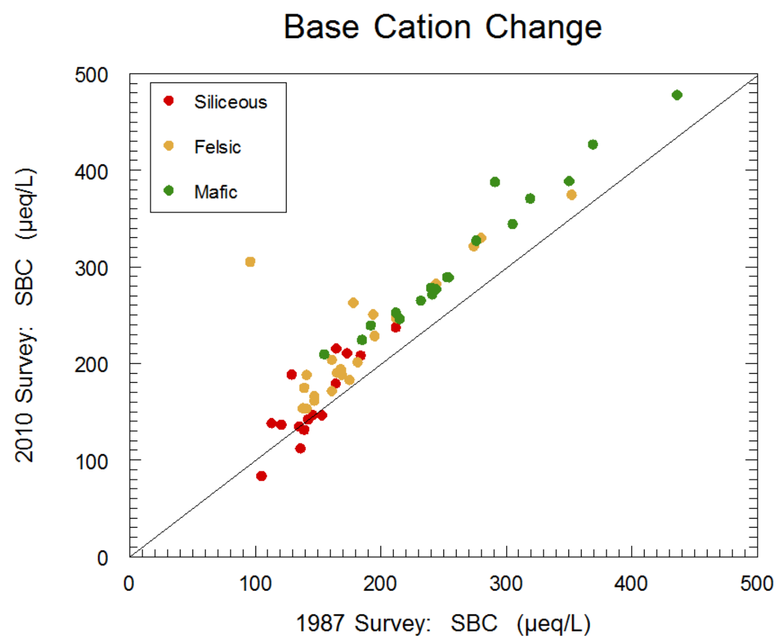


FIGURE 8 - *continued*

TABLE 4 - Relationship between watershed bedrock class and change in stream water concentrations measured in the 1987 and 2010 VTSSS surveys.[1]

Dependent Variable[2]	Intercept	% Siliceous[3]	% Felsic[3]	R^2	p-value
Change in ANC	81.2	-0.638	-0.344	0.304	0.000
Change in sulfate	-19.7	+0.026	+0.101	0.064	0.180
Change in base cations	55.1	-0.487	-0.202	0.222	0.001

[1] Determined by linear regression (SPSS, 2011).

[2] Change (µeq/L) between sites sampled in both the 1987 and 2010 surveys.

[3] Watershed bedrock classification is based on (Sullivan et al., 2007).

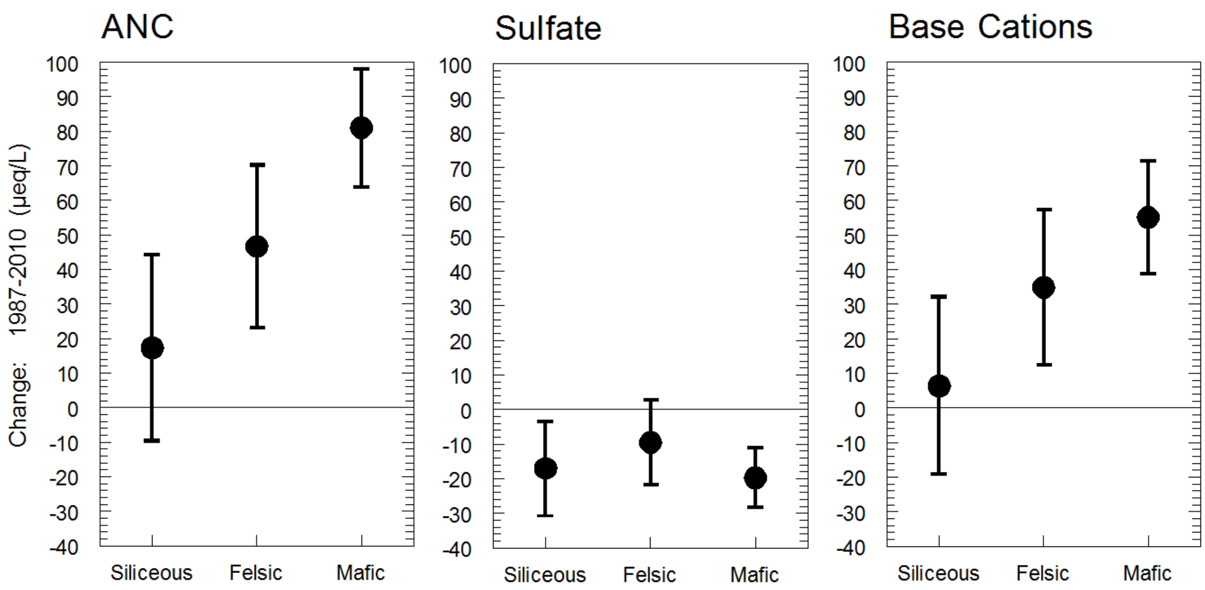


FIGURE 9 - Estimated means and 95% confidence intervals for change in acid-base chemistry between 1987 and 2010 for streams associated with single bedrock classes. Based on linear regression results (see Table 4).

A strong bedrock-related gradient is evident for the change observed in stream water ANC concentrations between the 1987 and 2010 VTSSS surveys. As expected based on critical loads and deposition-scenario modeling (Cosby et al., 2006; Sullivan et al., 2008), the least improvement in ANC is associated with siliceous bedrock. Moreover, the gradient in ANC change in relation to bedrock class conforms with the relationship observed between ANC and bedrock class in SHEN. This differs from findings for the larger VTSSS survey region. Miller (2011) did not find significant relationships between bedrock class and change in ANC concentrations between the 1987 and 2010 surveys. This difference may be explained by differences in bedrock mapping. Sullivan et al. (2007), for example, found that bedrock mapping discrepancies reduce the value of map-based bedrock classification as a tool for predicting ANC in the larger southern Appalachian Mountain region. This appears to be less of a problem in SHEN and the Blue Ridge Mountain Province than in the larger region.

The relationship between bedrock and change observed in stream water base cation concentrations between the 1987 and 2010 surveys is similar to that observed for ANC.

Although base cations are increasing in streams associated with all three bedrock classes, the increase is the least for streams associated with siliceous bedrock. This is consistent with the relationship between bedrock distribution and base cation concentrations in stream water, and it conforms with expectations based on both bedrock composition and base cation status in soils. As discussed in Section 4.1 of this report, however, a general increase in base cation concentrations concurrent with a decrease in sulfate concentrations is unexpected. Additionally, the pattern of change differs from that observed for the trend analyses reported by Sullivan et al. (2003). That analysis of SWAS quarterly sample data collected during the 1988-2001 period indicated positive trends in base cation concentrations for streams associated with mafic bedrock, but negative trends for streams associated with siliceous and felsic bedrock. In contrast, base cations increased in streams associated with all three bedrock classes between the 1987 and 2010 VTSSS surveys.

The relationship between bedrock and change in stream water sulfate concentrations between the 1987 and 2010 surveys is relatively weak compared to the relationships observed for change in ANC and base cations. This is related in part to the smaller change that occurred. Also, differing from ANC and related ions derived from watershed sources, variation in stream water concentrations of sulfate, which is derived from the atmosphere, is not as closely related to bedrock distribution. Sulfate concentrations are instead determined by sulfur retention in soils, and although soils in SHEN are mostly developed from underlying bedrock, general correlations between sulfate concentrations in streams and watershed bedrock have not been observed in studies of stream chemistry and bedrock relationships (e.g., Lynch and Dise, 1985).

5.2 Other Watershed Variables

The other variables considered are watershed elevation, watershed area, and forest disturbance (gypsy moth defoliation).

Differences in watershed elevation might affect stream response to changes in acidic deposition in a number of ways. Elevation has been associated with depositional gradients related to differences in precipitation amount and cloud or fog exposure. Cloud water can be more acidic than precipitation, and cloud exposure can be an important component of acidic deposition in some watersheds (Sullivan, 2000). The higher-elevation areas of mountain ridges also tend to have steeper slopes and shallower, less-developed soils relative to lower or down-slope areas. Relative to lower elevations, soils at higher elevations will thus tend have less water retention and shorter residence times, as well as less capability for neutralization of acidity through base cation exchange or sulfate retention. Miller (2011) observed a weak but significant association between elevation and the rate of recovery from acidification, with lower elevations sites showing slightly more recovery between the 1987 and 2010 VTSSS surveys.

Watershed area may also relate to differences in stream water response to changes in acidic deposition. Smaller watershed tend to occur at higher elevations than larger watersheds. Also, given the scale of spatial variation in bedrock and soil conditions in SHEN, smaller watersheds are more likely to be associated with less variation in bedrock and soil types. Streams associated with larger watersheds, in contrast, are more likely to integrate the effects of multiple bedrock and soil types. The population of streams associated with small watersheds may thus represent a broader range in acid-base status than larger streams.

The effect of forest defoliation by the larva of the gypsy moth (*Lymantria dispar*) on stream water composition in SHEN has been extensively studied (Webb, et al., 1995; Eshleman et al., 1998; Eshleman et al., 2001). Between the mid-1980s and the early 1990s, the southward expanding range of the gypsy moth affected all of the SWAS and VTSSS study watersheds in SHEN. Severe and repeated forest defoliation occurred in some watersheds, and localized outbreaks have continued to occur. The most substantial effect on stream water chemistry was a dramatic increase in concentrations of nitrate, which then declined over 5-10 years following defoliation. Prior to the defoliation nitrate concentrations typically were near-zero in SHEN streams. Additional effects of defoliation included an increase in base cation concentrations and a decrease in sulfate concentrations. These observable effects on stream water composition were largely over by 2000. The full effect of the gypsy moth on stream water composition in SHEN is not well understood.

The possible relationships between changes in ANC, sulfate, and the sum of base cations between the 1987 and 2010 VTSSS survey with watershed elevation (specifically the elevation of the stream sampling point), watershed area (defined by the sampling point), and forest defoliation (determined as cumulative percent watershed defoliation) was examined by regression analysis (Table 5). Based on this analysis, none of these variables are associated with variation in the observed change in stream water concentrations of ANC, sulfate, or the sum of base cations.

TABLE 5 - Relationships between landscape variables and change in stream water concentrations measured in the 1987 and 2010 VTSSS surveys.[1]

Independent Variable	Dependent Variable[2]	R^2	p-value	Equation
Watershed area[3]	Change in ANC	0.035	0.171	Y = 42.5 + 0.012X
Cumulative watershed defoliation[4]	Change in ANC	0.002	0.763	Y = 55.7 - 0.013X
Sample site elevation[5]	Change in ANC	0.012	0.418	Y = 34.2 + 0.011X
Watershed area[3]	Change in sulfate	0.003	0.700	Y = -14.1 - 0.001X
Cumulative watershed defoliation[4]	Change in sulfate	0.064	0.063	Y = -0.4 - 0.034X
Sample site elevation[5]	Change in sulfate	0.051	0.096	Y = -29.2 + 0.010X
Watershed area[3]	Change in base cations	0.010	0.471	Y = 30.2 + 0.006X
Cumulative watershed defoliation[4]	Change in base cations	0.032	0.189	Y = 55.3 - 0.050X
Sample site elevation[5]	Change in base cations	0.078	0.039	Y = -2.4 + 0.026X

[1] Determined by linear regression (SPSS, 2011).

[2] Change (µeq/L) between sites sampled in both the 1987 and 2010 surveys.

[3] Watershed area (km^2) above stream sampling points.

[4] Cumulative percent watershed defoliation based on available annual defoliation data for 1986-2009. Data source: Virginia Department of Forestry.

[5] Feet above mean sea level.

6.0 SUMMARY OF OBSERVATIONS

- Stream water samples were collected for analysis of acid-base chemistry from 458 sites on native brook trout streams in the western Virginia mountains during the VTSSS survey conducted in the spring of 2010. During the sample collection window, 66 sites were sampled on streams in SHEN or on streams that flow out of the park, including 14 sites that were sampled as part of routine monitoring by the SWAS program (eight quarterly and six weekly). Of these sites sampled in the 2010 survey, 55 were also sampled in the previous 1987 and 2000 surveys.

- A comparison of median ANC, sulfate, and the sum of base cation concentration values for the 66 SHEN survey sites and the other 376 regional survey sites indicates that only the values for ANC were statistically different. For SHEN sites, the median ANC concentration was 124.5 µeq/L; for the other regional survey sites, the median ANC concentration was 93.6 µeq/L. The higher ANC observed for SHEN streams is consistent with differences in bedrock distribution.
- Comparison of ANC, sulfate, and base cation concentrations for the 1987 and 2010 surveys for stream samples collected in or adjacent SHEN (n = 55), indicates that the median of stream ANC concentrations increased 59% (45.0 µeq/L), the median of stream sulfate concentrations declined 20% (16.5 µeq/L), and the median of stream base cation concentrations increased 21% (31.5 µeq/L).
- Most of the observed change in stream water concentrations of ANC and sulfate occurred between samples collected in 2000 and 2010. Most of the observed change in stream water concentrations of base cations occurred between samples collected in 1987 and 2000.
- The timing of the largest change in ANC and sulfate concentrations in stream water coincided with the lowest recorded levels of sulfate deposition and highest recorded rate of decrease in sulfate deposition in precipitation at the NADP Big Meadows deposition monitoring site in SHEN.
- Although the observed changes in stream water ANC and sulfate concentrations are consistent with recovery from acidification caused by acidic deposition, the concurrent increase in base cation concentrations indicate that factors other than reduced acidic deposition are responsible for part of the increase in ANC. The current level of recovery may not be sustained if the increase in base cations proves temporary. Moreover, the evident increase in the export of base cations in stream water may be associated with accelerated depletion of the supply of available base cations in watershed soils, which would diminish the prospect for long-term recovery.
- Relative to the ANC concentration of 50 µeq/L, a commonly applied reference value for biological effects of acidification, substantial improvement was observed in SHEN streams

between the 1987 and 2010 surveys. In 1987, the number of streams with ANC < 50 μeq/L was 17, or 34.0% of the total number of streams sampled in both the 1987 and 2010 surveys. In 2010, the number of streams with ANC < 50 μeq/L decreased to 9, or 16.4% of the surveyed streams. All of the streams with ANC < 50 μeq/L in 2010 drain watersheds that are predominantly (at least 87%) underlain by relatively base-poor siliceous (siliciclastic) bedrock.

- Strong bedrock-related gradients are evident for the changes observed in both stream water ANC and sum of base cation concentrations between the 1987 and 2010 VTSSS surveys. Although ANC and base cations are increasing in streams associated with all three bedrock classes, the increase is the least for streams associated with siliceous bedrock and the most for streams associated with mafic bedrock. This relationship between change and bedrock is consistent with the strong relationship between concentration and bedrock.
- The relationship between bedrock and change in stream water sulfate concentrations between the 1987 and 2010 surveys is relatively weak compared to the relationships observed for change in ANC and base cations. This is related to the smaller change that occurred and to the relatively weak correlation between stream water sulfate concentration and bedrock.
- No association was observed between change in stream water ANC, sulfate, and base cation concentrations and other landscape variables that were considered, including watershed elevation, watershed area, and cumulative percent watershed defoliation.

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