

Long-term response of surface water acid neutralizing capacity in a central Appalachian (USA) river basin to declining acid deposition



Kathleen M. Kline ^{a,*}, Keith N. Eshleman ^a, James E. Garlitz ^a, Sarah H. U'Ren ^b

^a Appalachian Laboratory, University of Maryland Center for Environmental Science, 301 Braddock Road, Frostburg, MD 21532, USA

^b The Watershed Center of Grand Traverse Bay, 13272 S W Bay Shore Dr., Traverse City, MI 49684, USA

HIGHLIGHTS

- Data from multiple synoptic spring baseflow surveys were used to characterize the acid-base status of USRW streams.
- Decreasing trends in surface water SO_4^{2-} and NO_3^- were explained by declining S and N emissions and deposition onto USRW.
- We observed significant ANC recovery in 10–20% of the USRW stream network, despite not detecting a regional ANC trend.
- Surface water ANC recovery was significantly moderated by decreasing trends in K^+ , Mg^{2+} , and Ca^{2+} concentrations.
- RKT appears to be a robust method for identifying basin-wide trends for some key chemical constituents.

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ABSTRACT

Long-term changes in acid-base chemistry resulting from declining regional acid deposition were examined using data from repeating synoptic surveys conducted within the 275 km² Upper Savage River Watershed (USRW) in western Maryland (USA); a randomly-selected set of 40 stream reaches was sampled 36 times between 1999 and 2014 to: (1) repeatedly characterize the acid-base status of the entire river basin; (2) determine whether an extensive network of streams of varying order has shown signs of recovery in acid neutralizing capacity (ANC); and (3) understand the key factors controlling the rate of ANC recovery across the river network. Several non-parametric analyses of trends (i.e., Mann Kendall Trend: MKT tests; and Regional Kendall Trend: RKT) in streamwater acid-base chemistry suggest that USRW has significantly responded to declining acid deposition during the study period; the two most robust, statistically significant trends were decreasing surface water SO_4^{2-} ($\sim 1.5 \mu\text{eq L}^{-1} \text{yr}^{-1}$) and NO_3^- ($\sim 1 \mu\text{eq L}^{-1} \text{yr}^{-1}$) concentrations—consistent with observed downward trends in regional wet S and N deposition. Basin-wide decreasing trends in K^+ , Mg^{2+} , and Ca^{2+} were also observed, while Na^+ concentrations increased. Significant ANC recovery was observed in 10–20% of USRW stream reaches (depending on the p level used), but the magnitude of the trend relative to natural variability was apparently insufficient to allow detection of a basin-wide ANC trend using the RKT test. Watershed factors, such as forest disturbances and increased application of road deicing salts, appeared to contribute to substantial variability in concentrations of NO_3^- and Na^+ in streams across the basin, but these factors did not affect our overall interpretation of the results as a systematic recovery of USRW from regional acidification. Methodologically, RKT appears to be a robust method for identifying basin-wide trends using synoptic data, but MKT results for individual systems should be examined closely (e.g., to identify trends for specific subpopulations).

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Abbreviations: CAAA, U.S. Clean Air Act Amendments of 1990; SO_2 , sulfur dioxide; NO_x , nitrogen oxide; μeq , microequivalents; ANC, acid neutralizing capacity, $\mu\text{eq L}^{-1}$; DOA, dissolved organic acids, $\mu\text{eq L}^{-1}$; DOC, dissolved organic carbon, mg L^{-1} ; SBC, sum of base cations, ($\text{Na}^+ + \text{K}^+ + \text{Mg}^{2+} + \text{Ca}^{2+}$), $\mu\text{eq L}^{-1}$; MKT, Mann-Kendall Trend Test; RKT, Regional Kendall Trend Test; USRW, Upper Savage River Watershed; NADP, National Atmospheric Deposition Program; DI, Disturbance Index.

* Corresponding author.

E-mail address: kkline@al.umces.edu (K.M. Kline).

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1. Introduction

Atmospheric deposition of acidifying pollutants originating primarily from fossil fuel combustion contributed to acidification of surface waters in many regions of Europe and North America during the 20th century (Sullivan et al., 1988; Kaufmann et al., 1991; Herlihy et al., 1991). Title IV of the Clean Air Act Amendments (CAAA) of 1990 reduced emissions of SO₂ and NO_x from stationary electricity-generation sources in the United States (U.S.), resulting in reductions in wet deposition of acidifying pollutants, as well as in the acidity of precipitation, throughout much of the country (Lynch et al., 2000). By the late 1990s, these emission controls had led to ~40% reductions in sulfate deposition in the eastern U.S. with the greatest improvements observed in the mid-Appalachian mountain region (Burns et al., 2011). Furthermore, other regulatory programs implemented in the late 1990s and early 2000s (e.g., Ozone Transport Commission NO_x Budget Trading Program, the NO_x State Implementation Plan Call, the Clean Air Interstate Rule, the Cross-State Air Pollution Rule, as well as improved vehicle emission standards) effectively controlled NO_x emissions from both stationary and mobile sources, contributing to reductions in NO₃ deposition (Butler et al., 2011). By 2009, reductions of approximately 27% in inorganic N deposition had been observed in the eastern U.S. (Burns et al., 2011); more recently, even greater (32–47%) reductions in inorganic N deposition were reported for some high elevation subwatersheds and major tributaries, as well as the main stem, of the Potomac River (Eshleman and Sabo this issue).

Implementation of emission controls produced almost immediate declines in surface water sulfate concentrations, especially in the northeastern U.S., Canada, and Europe, as well as decreases in surface water nitrate concentrations in some studies (Clow and Mast, 1999; Stoddard et al., 1999; Driscoll et al., 2003; Kahl et al., 2004; Eshleman et al., 2013; Eshleman and Sabo, this issue). In some cases, reductions in acid anion concentrations in surface waters contributed to modest recovery in acid neutralizing capacity (ANC), such as in an intensively-monitored first order stream in Savage River watershed on the Appalachian Plateau of western Maryland (Eshleman et al., 2008). Previous analyses have suggested a recovery rate of ANC for this region of about 1.5 $\mu\text{eq L}^{-1} \text{yr}^{-1}$ (Skjelkvale et al., 2005; Stoddard et al., 2003; Eshleman et al., 2008). In contrast, ANC recovery in streams has not been observed at other locations, particularly in the glaciated northeastern U.S. and the southeastern U.S., where it has been hypothesized that concomitant decreases in base cation deposition (Likens et al., 1996; Clow and Mast, 1999; Stoddard et al., 1999); increases in surface water dissolved organic carbon (DOC) (Evans et al., 2006; Erlandsson et al., 2011); decreasing surface water base cation concentrations from depleted soil base saturation (Lawrence et al., 1999; Driscoll et al., 2001); or soil sulfate sorption (Cosby et al., 1986, 2001) have limited or delayed recovery.

Prior ANC recovery studies conducted in the late 1990s and early 2000s focused primarily on either a few individual stations (Likens et al., 1996; Eshleman et al., 2008) or multiple stations throughout relatively large regions (Clow and Mast, 1999; Stoddard et al., 1999; Kahl et al., 2004; Skjelkvale et al., 2005; Garmo et al., 2014; Strock et al., 2014). Our objectives in this study were to: (1) repeatedly characterize the acid-base status of an entire river basin over a 15-year period; (2) determine whether an extensive network of streams of varying order within a single river basin has shown signs of ANC recovery from earlier acidification during a period of dramatic declines in sulfuric and nitric acid deposition; and (3) understand the key factors controlling the rate of ANC recovery from acidification across a stream network.

2. Materials and methods

We examined recovery trends for a random sample of stream reaches of varying order (1st through 4th) in the Upper Savage River Watershed (USRW) located on the rugged Appalachian Plateau in western Maryland, USA (Fig. 1). Geographically, Savage River is a major tributary of the North Branch of the Potomac River. The USRW covers an area of 275 km² in the headwaters of Savage River upstream of Savage River Dam and Reservoir; the basin is bordered by Meadow Mountain to the west and by Big Savage Mountain to the east, and is situated on a fluvially-dissected anticline consisting of gently-folded sedimentary rocks of Permian, Pennsylvanian, and Mississippian age (Brezinski and Conkwright, 2013). The basin is minimally populated and mostly undeveloped; 80% is forested, 15% is in agriculture, and there are only a few small developed areas (<5%) within USRW. Savage River State Forest covers 46% of the basin.

Thirty-six repeating, synoptic stream surveys were conducted between 1999 and 2014 at 40 randomly-selected stream reaches within the USRW (Hypio, 2000). The survey design was based on 1:24,000-scale digital river reach data included in the National Hydrography Dataset for the USA (www.nhd.usgs.gov) with the 40 reaches selected randomly from the entire digital stream network for the USRW (grouped by major subwatershed to ensure broad geographic representation) with the probability of selecting a particular reach proportional to the individual reach length (Hypio, 2000). With the exception of a few surveys intentionally conducted under stormflow conditions, all of the field sampling was performed under seasonal baseflow conditions (using on-line discharge data from a USGS station within the watershed to ensure that baseflow conditions prevailed during sampling). Each survey was normally completed in either one day or on two consecutive days to minimize the effects of hydrologic variations on water chemistry; for consistency, all water samples were collected at fixed locations at, or near (in the few cases where logistics prohibited it), the downstream end of each stream reach.

“Grab” water samples were collected in triple-rinsed, 1L polyethylene cubitainers and kept on ice in a cooler until returned to the laboratory where they were filtered (0.45 μm membrane) for analysis of acid anions (chloride, Cl⁻; nitrate, NO₃⁻; sulfate, SO₄²⁻ by ion chromatography), base cations (sodium, Na⁺; potassium, K⁺; magnesium, Mg²⁺; calcium, Ca²⁺ by flame atomic absorption spectrometry), and dissolved organic acids (DOA) estimated from dissolved organic carbon (DOC by UV-assisted persulfate digestion) using the model of Oliver et al. (1983); specific conductance (conductivity meter; $\mu\text{S/cm}$) and acid neutralizing capacity (ANC by automated, acidimetric Gran titration) were measured on unfiltered aliquots. Blanks and independent check samples were used in each batch to ensure that our analyses met rigorous quality control standards. Conductivity and ion balance calculations were used as internal quality control checks.

Since the various surveys were conducted on an irregular basis, we relied on long-term water chemistry data from two intensively-monitored, gaged subwatersheds nested within the USRW (Upper Big Run: BIGR; area = 162 ha and Black Lick: BLAC; area = 558 ha) to determine which synoptic surveys were likely to provide data that were most representative of annual average conditions. BIGR was selected for long-term study because of its extreme acid sensitivity (ANC < 50 $\mu\text{eq L}^{-1}$), while BLAC was determined to exhibit less acid sensitivity (100 $\mu\text{eq L}^{-1}$ < ANC < 200 $\mu\text{eq L}^{-1}$). While both watersheds are predominantly forested, neither is pristine; BIGR is bisected by a county-maintained road and a power line corridor, while BLAC has considerable agricultural land in its headwaters. Monthly and annual discharge-weighted mean concentrations for major chemical constituents were estimated using

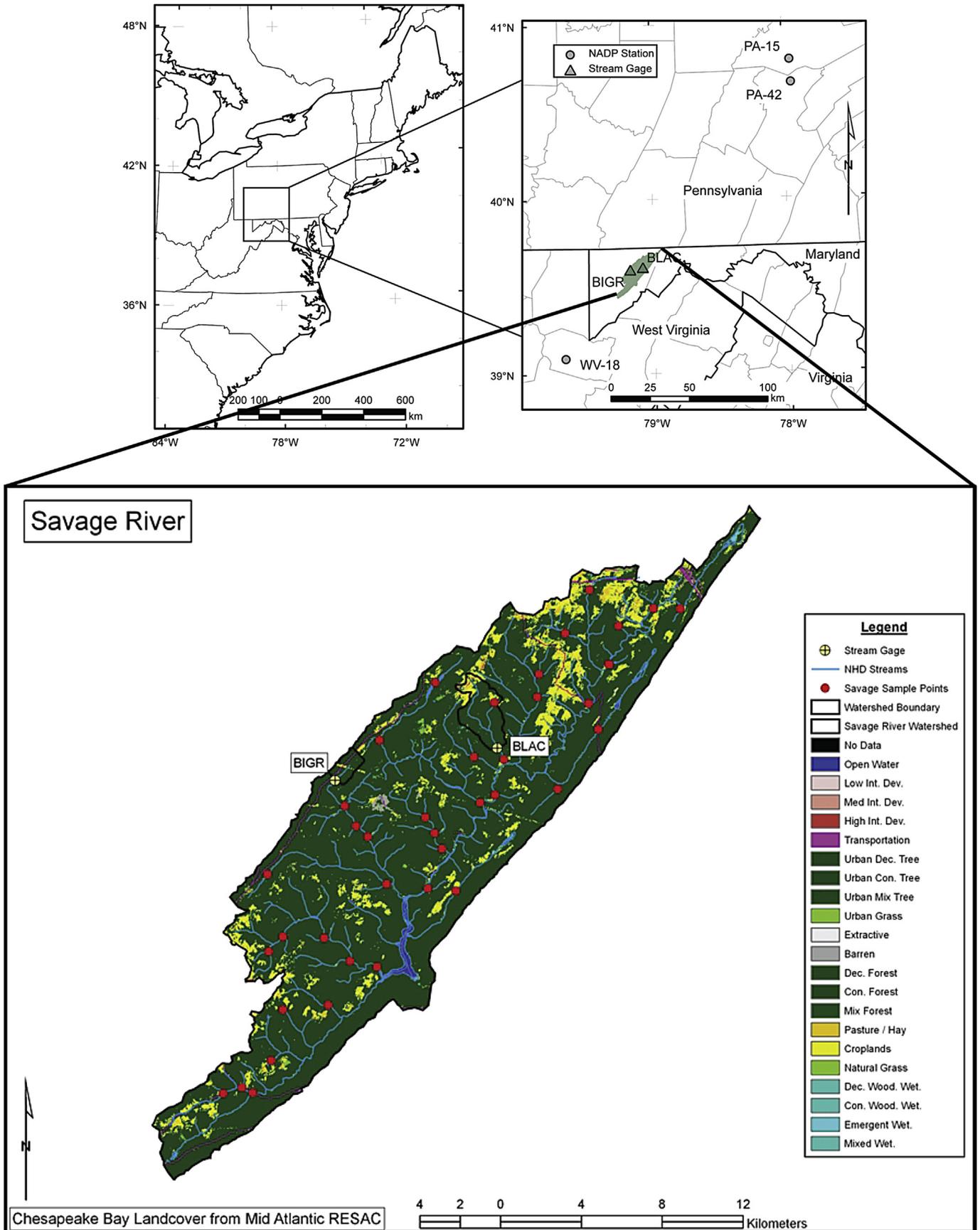


Fig. 1. Site locations for the 40 synoptic survey reaches and two gaged and intensively-monitored subwatersheds (BIGR, BLAC). USRW land use/land cover and locations of three NADP wet deposition monitoring stations are also shown.

long-term (BIGR: 1990–2013; BLAC: 1997–2013) discharge and concentration data and a seven-parameter load estimation model known as LOADEST (Cohn et al., 1989; Runkel et al., 2004; Eshleman et al., 2008). We calculated the arithmetic difference between monthly discharge-weighted mean concentrations and the annual discharge-weighted mean concentration for each year within the long-term record; mean differences (and 95% confidence intervals) for each month were computed as a way of assessing the bias and relative predictability associated with conducting synoptic sampling during different months of the year.

Trends in annual concentrations at the 40 synoptic sites within USRW (as well as comparable data for BIGR and BLAC) were analyzed for statistical significance ($p \leq 0.05$) using the nonparametric Mann-Kendall Trend (MKT) test with Sen's Slope estimator (Mann, 1945; Sen, 1968) with the TimeTrends software program (Jowett, 2009); the same approach was used to examine trends in the same constituents measured at BIGR and BLAC as well. For the synoptic data, a χ^2 test for homogeneity of trends between stations (van Belle and Hughes, 1984) was performed for each parameter to determine objectively whether any trends were consistent among sampled sites within USRW. The station homogeneity test uses the Mann-Kendall statistics computed for each station to quantitatively test for homogeneity of trend direction at multiple stations. Trends were considered to be homogeneous basin-wide if the χ^2 homogeneity value was less than the critical value for 39 degrees of freedom (df) ($p \leq 0.001$). For those constituents within USRW that exhibited homogeneity of stations, the χ^2 statistic for the trend was calculated and compared to the chi-square distribution for 1 df to determine whether the trend direction was significantly different from zero. For parameters that passed the station homogeneity test, results from the MKT were combined to perform a Regional Kendall Trend (RKT) analysis (Helsel and Frans, 2006); by substituting location for season in a Seasonal Kendall test (Hirsch et al., 1982; Helsel and Hirsch, 2002), RKT allowed us to determine the central tendency of each trend and estimate a Sen slope.

To help understand the surface water trends, we used the same statistical methodology to investigate trends in annual wet deposition for the same time period using data reported for three National Atmospheric Deposition Program (NADP, 2015) stations located in the mid-Appalachian region: two stations (PA-15, PA-42) are located in central Pennsylvania northeast of USRW and one station (WV-18) is located in West Virginia southeast of the basin (Fig. 1). Statistical tests were performed on mean annual depth-weighted concentrations computed for each constituent. Since ANC is not measured by NADP, we inferred ANC from the reported pH data (i.e., $\text{ANC} = 10^{-(\text{pH})}$, which is typically valid if $\text{ANC} < 0$).

3. Results and discussion

Percent bias associated with estimating annual discharge-weighted mean concentrations of NO_3^- , SO_4^{2-} , ANC, and sum of base cations ($\text{SBC} = \text{Na}^+ + \text{K}^+ + \text{Ca}^{2+} + \text{Mg}^{2+}$) for BIGR and BLAC varied dramatically across the year (Fig. 2); due to relatively consistent intra-annual variability in these constituent concentrations, however, the graphs for each constituent show a “cross-over” pattern in which percent bias is (statistically) expected to be zero twice during the year. Percent bias patterns were most similar for NO_3^- and ANC, with positive sampling bias observed in the winter/early spring period for NO_3^- and negative sampling bias observed in the winter/early spring for ANC at both sites. Estimated percent bias for SO_4^{2-} was much lower, especially for BLAC where it was less than $\pm 5\%$ during all months. At BIGR, however, percent bias for SO_4^{2-} was as great as -30% to -40% during the summer months. Percent bias for SBC was highly variable between the sites, with the two watersheds exhibiting opposite patterns of positive and negative

percent bias during the year (although the timing of the “cross-overs” remained fairly consistent). While not totally consistent between the constituents and among the sites, visual inspection of the graphs showed that for these four constituents, the two cross-over times that minimize sampling bias are late fall (typically November or December) and late spring (typically April and May). Since a secondary goal was to identify the timing of sampling with highest expected predictability (i.e., lowest variability) in estimating annual average conditions, we determined that the spring months (April, May, and June) produced consistently smaller confidence intervals compared to the autumn months (Fig. 2). Based on the results of the percent bias analysis, we made the decision to base our long-term trend analyses solely on 21 baseflow surveys that were conducted during the mid-to late-spring period; data from the other 15 surveys were only used to help interpret the trends. We found few rigorous analyses of temporal sampling bias in the literature against which we could compare our results, but we note that several regional stream surveys conducted by USEPA back in the 1980s utilized spring baseflow sampling to provide a suitable “index” of annual chemical conditions (Messer et al., 1986; Kaufmann et al., 1991). In each of those surveys, samples were collected under baseflow conditions between spring snowmelt and leaf-out, while intentionally avoiding the influence of high flow conditions that can cause episodic acidification (Wigington et al., 1990; Davies et al., 1992). For the dates associated with the spring baseflow surveys, mean daily discharge monitored at long-term USGS station #01596500 (Savage River near Barton, MD) averaged 1.64 cms (95% c.i. = ± 0.53 cms), indicating that only a few of our surveys were conducted under flow conditions that varied more than $\pm 33\%$ from the mean; the mean daily discharge at this station during the 21 surveys was actually about 25% lower than the long-term (1949–2014) mean discharge (2.44 cms) based on data from the same gaging station.

Data from BIGR and BLAC were used to provide a second test of whether trend analysis for the synoptic stations could be accomplished by relying solely on the spring baseflow surveys; we thus compared MKT results based on “raw” spring (April, May, and early June) baseflow concentrations with MKT results based on annual discharge-weighted mean concentration values using LOADEST. Trend direction and magnitude were very similar for most of the constituents (with the exception of Ca^{2+} for BIGR and Cl^- for BLAC), suggesting that our proposed method of stratifying and analyzing the data from the synoptic stations was the least biased approach given the irregularities in the timing of data collection (Fig. 3).

Simple frequency distributions of raw constituent concentrations measured in spring 1999 and 2014 suggest major shifts over time in ANC, NO_3^- , and SO_4^{2-} concentrations across the stream network (Fig. 4). More than 70% of the streams sampled in 1999 had an ANC less than $100 \mu\text{eq L}^{-1}$, while more than 75% of the sites had an ANC greater than $100 \mu\text{eq L}^{-1}$ in 2014. Corresponding shifts were also observed for both SO_4^{2-} and NO_3^- concentrations in the streams, suggesting the possibility of long-term monotonic responses to decreasing deposition of acidifying pollutants in the region. Annual discharge-weighted mean concentrations for the two intensively-monitored streams confirm that BIGR falls into the extremely acid-sensitive class of stream reaches with lower ion concentrations, while BLAC falls into a less acid sensitive class with higher ion (especially base cation) concentrations (Fig. 4).

Regardless of the significance of any trends, most of the stream network in USRW can be characterized as acid-sensitive using a commonly accepted definition of $\text{ANC} < 200 \mu\text{eq L}^{-1}$. Data for the 40 synoptic stations represent a fairly wide range in ANC (and a corresponding range in major ion concentrations; Fig. 4), however. Acid anions are dominated by SO_4^{2-} and NO_3^- which also dominate wet deposition in the Appalachian region, with only a few

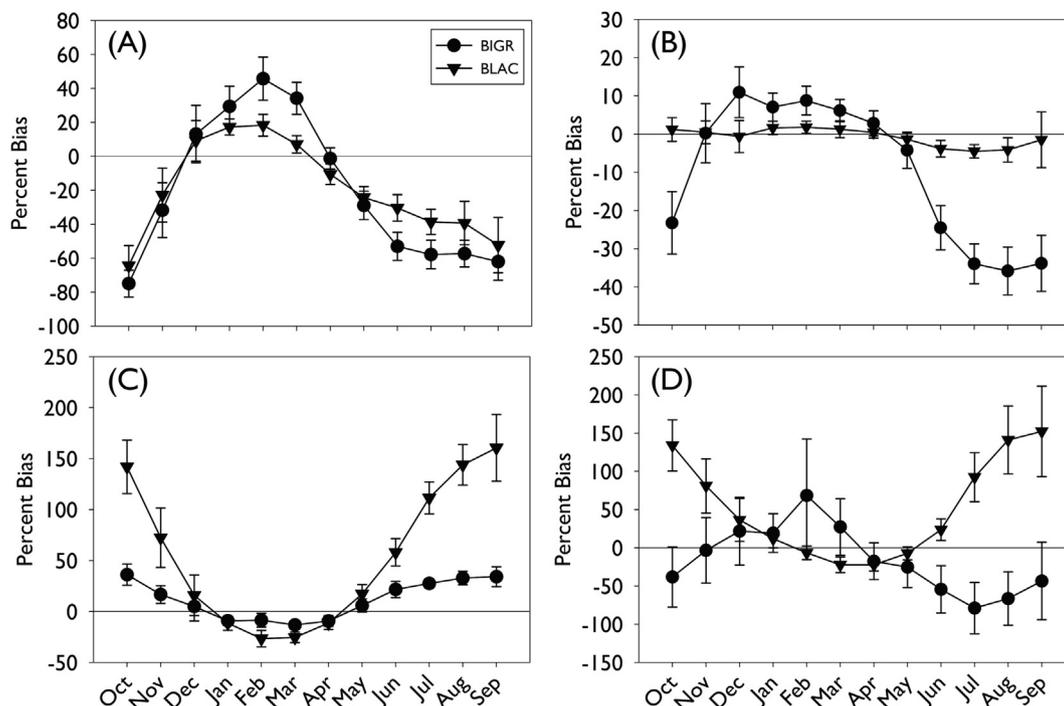


Fig. 2. Percent bias (means and 95% confidence intervals) for (A) NO_3^- , (B) SO_4^{2-} , (C) ANC, and (D) SBC for the two intensively-monitored watersheds.

headwater streams containing appreciable concentrations of DOA. Spatial variation in streamwater ANC is presumably controlled largely by the weathering reactions associated with the interaction of water precipitated onto the land with the minerals that comprise the sedimentary bedrock geology underlying a complex mountainous terrain; although dominated by sandstones and shales, USRW includes a relatively small, but not insignificant, area of outcropping limestone bedrock (Greenbrier Formation). The USRW falls within the eastern mountain section of the Appalachian Plateau physiographic province (Fenneman 1938)—due to the fact that the sedimentary bedrock underlying the basin has undergone significant folding, as well as fluvial dissection, complicating both hydrologic flowpaths and the water–rock interactions noted above. The topography is such that the majority of agricultural and developed land is situated on the plateau itself, while steeply sloping land in USRW is almost completely forested (Fig. 1).

Mann–Kendall trend results for individual surface water stations are summarized by constituent in the Supplementary Data (Tables S1 through S10). Prior to performing the test for homogeneity of stations, we qualitatively examined time series plots of raw concentrations for the individual sites over time (including data from the 21 spring baseflow surveys used for the MKT, as well as the 15 other surveys) in relation to the derived MKT trend line. As a representative example, results from the first order, predominantly-forested (~80%) BBL112 site show decreasing trends for Cl^- , NO_3^- , SO_4^{2-} , Mg^{2+} , and Ca^{2+} with no significant trends for DOA, Na^+ , or K^+ (Fig. 5). While the data corresponding to the unused points (open symbols) for K^+ , DOA, Mg^{2+} , Ca^{2+} , and SO_4^{2-} were distributed reasonably closely to the trend line, somewhat greater variability was observed for ANC, NO_3^- , and Na^+ . As illustrated in Fig. 2, concentrations of ANC and NO_3^- are strongly dependent on season and flow conditions; NO_3^- concentrations can also be an indicator of land use changes (Donner et al., 2004; Johnson et al., 2007), watershed management (Weller et al., 2011), or natural disturbances (Eshleman et al., 1998) in a particular watershed. These results help to further illustrate that confining our statistical

analysis of trends to the spring baseflow survey data likely contributed to reducing bias and improving trend detectability.

The next step in our analysis was performing the station homogeneity tests for USRW to quantitatively assess our ability to make basin-wide or regional statements about trends. The results indicated homogeneity of trends by station for the following constituents: ANC, NO_3^- , SO_4^{2-} , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and DOA ($p \leq 0.001$). Among these constituents, all except ANC demonstrated trends significantly different from zero using the χ^2 statistic ($p \leq 0.05$; Table 1). Therefore, we conclude that RKT analysis is an appropriate technique for estimating regional trends for these constituent concentrations and for allowing us to draw basin-wide conclusions about the trends. RKT was thus used to assess trends in surface water concentrations for those constituents that passed the χ^2 tests for homogeneity and trend. RKT results based on data from the 40 stations suggested statistically significant ($p \leq 0.05$) regional (i.e., basin-wide) trends for six constituents: NO_3^- , SO_4^{2-} , K^+ , Mg^{2+} , Ca^{2+} , and Na^+ . Trends for five of the six constituent concentrations (all except Na^+) were downward. Sen slopes for these trends were -0.8 , -1.5 , -0.3 , -0.8 , and $-2.5 \mu\text{eq L}^{-1} \text{yr}^{-1}$ for NO_3^- , SO_4^{2-} , K^+ , Mg^{2+} , and Ca^{2+} concentration, respectively; the Sen slope of the trend for Na^+ concentration was $+1.1 \mu\text{eq L}^{-1} \text{yr}^{-1}$ (Table 2). These slopes can be combined to illustrate why no basin-wide trend was likely observed for ANC: the sum of the slopes of the base cation trends less the sum of the slopes of the acid anion trends = $-2.5 - (-2.3) = -0.2 \approx 0 \mu\text{eq L}^{-1} \text{yr}^{-1}$ suggests that the basin-wide decrease in acid anions was almost exactly balanced by a decrease in base cation concentrations.

Results from the station homogeneity test for the three central Appalachian NADP wet deposition stations (Fig. 1) indicated homogeneity of trends for inferred ANC, Cl^- , NO_3^- , SO_4^{2-} , K^+ , Mg^{2+} , and Ca^{2+} concentrations ($p \leq 0.001$; Table 1). Among these constituents, inferred ANC, Cl^- , NO_3^- , and SO_4^{2-} demonstrated trends significantly different from zero ($p \leq 0.05$). Therefore, RKT analysis could be used to assess trends in depth-weighted concentrations of inferred ANC, Cl^- , NO_3^- , and SO_4^{2-} , but no conclusions could be made

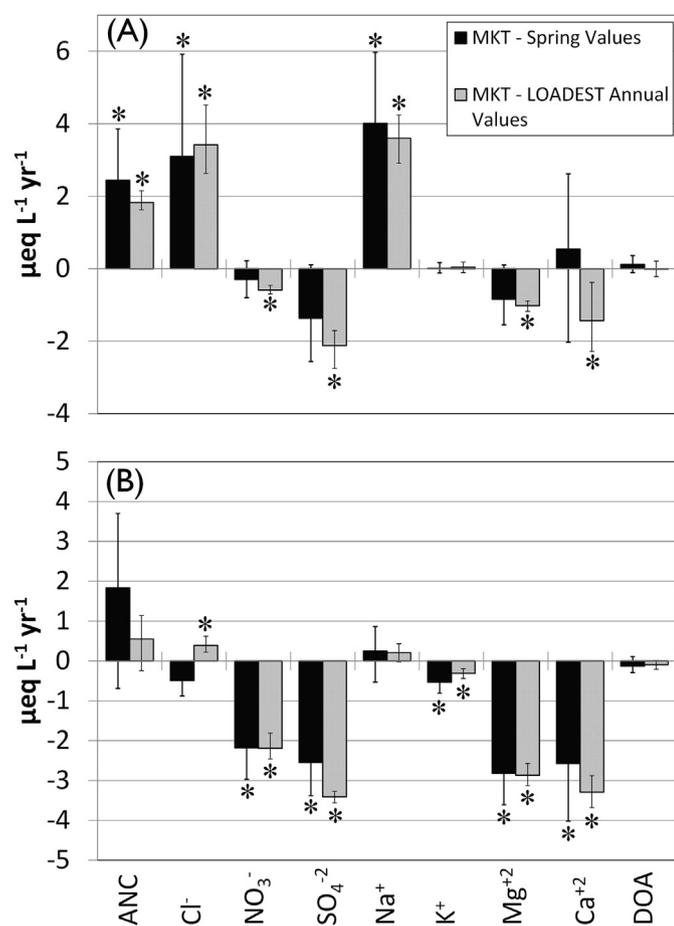


Fig. 3. Comparison of MKT results (Sen slopes; 95% confidence intervals) for nine chemical constituents for (A) BIGR and (B) BLAC using two different data sets: (1) “raw” spring (April, May, and early June) baseflow concentrations; and (2) annual discharge-weighted mean concentrations generated using LOADEST. Trends labeled with special symbol (*) are statistically significant ($p \leq 0.05$).

for any of the measured base cation (NH_4^+ , Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) concentrations. RKT analysis was performed to determine the central tendency of the trend for those constituents in wet deposition that passed the station homogeneity test (i.e., inferred ANC, Cl^- , NO_3^- , and SO_4^{2-}); trends for all four constituents were statistically significant ($p \leq 0.05$). Regional trends for Cl^- , NO_3^- , and SO_4^{2-} concentrations were all decreasing, but the trend for Cl^- ($0.1 \mu\text{eq L}^{-1} \text{yr}^{-1}$)—while significant—was negligible. NO_3^- showed a decreasing trend of about $1 \mu\text{eq L}^{-1} \text{yr}^{-1}$, while SO_4^{2-} demonstrated a decreasing trend of about $2 \mu\text{eq L}^{-1} \text{yr}^{-1}$. The trend for annual depth-weighted mean ANC (inferred from H^+ concentration in wet deposition) was positive with a slope of $2.6 \mu\text{eq L}^{-1} \text{yr}^{-1}$ (Table 2). Other recent work has demonstrated comparable trends for NO_3^- and SO_4^{2-} in wet deposition in the eastern US between 1970 and 2010, ranging from -0.7 to $-1.5 \mu\text{eq L}^{-1} \text{yr}^{-1}$ and -1.2 to $-1.9 \mu\text{eq L}^{-1} \text{yr}^{-1}$, respectively (Lajtha and Jones, 2013; Mast, 2013; Strock et al., 2014). Trends observed in these studies for annual depth-weighted mean ANC inferred from H^+ concentrations are somewhat lower than our estimate of $2.6 \mu\text{eq L}^{-1} \text{yr}^{-1}$, ranging from 1.5 to $1.8 \mu\text{eq L}^{-1} \text{yr}^{-1}$ for individual NADP stations in Pennsylvania and West Virginia, but our period of analysis of wet deposition trends covered only the years for which we had synoptic streamwater data from USRW.

Analyses of trends in stream water acid-base chemistry in USRW during the period 1999–2014 suggest that the basin has responded to declining acid deposition—the latter trend based on regional

NADP data. The two most robust, statistically significant trends that we observed in the synoptic survey results were declining SO_4^{2-} ($\sim -1.5 \mu\text{eq L}^{-1} \text{yr}^{-1}$) and NO_3^- ($\sim -1 \mu\text{eq L}^{-1} \text{yr}^{-1}$) concentrations; not only was the *direction* of change in these constituents completely consistent with the deposition trends, but the actual trends (slopes) were similar in *magnitude* to the deposition trends (Table 1)—suggesting that atmospheric deposition of both constituents is the primary controller of surface water concentrations in this basin. Numerous studies have implicated SO_4^{2-} deposition as the primary driver of surface water SO_4^{2-} concentrations in many regions of the U.S. (Fisher et al., 1968; Stam et al., 1992; Herlihy et al., 1993) and our data from this central Appalachian Mountain basin are consistent with this interpretation. Only more recent studies have implicated NO_3^- deposition as a major driver of surface water NO_3^- concentrations, and our synoptic survey results are consistent with analyses for other Appalachian Mountain basins documenting dramatic ($\sim 40\%$) declines in both N deposition and surface water NO_3^- concentrations beginning in the mid-1990s and continuing through 2012 (Eshleman et al., 2013; Eshleman and Sabo this issue). All of these observations appear to support a kinetic N saturation mechanism in which surface water NO_3^- concentrations are controlled by the atmospheric N deposition load, the rate of N aggradation by soils and vegetation on the watershed, and possibly a “non-responsive” or baseline NO_3^- load associated with agricultural management practices in the basin (Eshleman and Sabo this issue).

While SO_4^{2-} and NO_3^- trends in the synoptic results were both relatively robust, closer examination of the data showed substantial variability. While none of the 40 stations showed a statistically significant increasing trend for these constituents, the absolute range in SO_4^{2-} and NO_3^- trends among the synoptic stations actually ranged from -4.8 to $1.4 \mu\text{eq L}^{-1} \text{yr}^{-1}$ and -4.1 to $1.7 \mu\text{eq L}^{-1} \text{yr}^{-1}$ based on MKT (Fig. 6), respectively, demonstrating considerable intraregional variability. This variability was also evident in the trend results for the intensively monitored stations, BIGR and BLAC; both stations showed statistically significant decreasing long-term trends for both SO_4^{2-} and NO_3^- concentrations, but the trends deviated somewhat from the basin-wide trends (Table 2)—although they fell within the ranges shown in Fig. 6. Eshleman and Sabo (this issue) interpreted long-term NO_3^- trends for 18 watersheds in the context of the kinetic N saturation model. Relying on the same conceptual model, it appears that the more forested BIGR, with a higher rate of N retention owing to extensive defoliation by the gypsy moth caterpillar and salvage harvesting in the late 1980s, has a consistently lower NO_3^- concentration trend than BLAC (Fig. 3), the latter characterized by a greater percentage of agricultural land in its headwaters (and an inherently lower rate of N retention).

Another factor that may account for some of the spatial variation in the NO_3^- concentration trends was a second widespread gypsy moth defoliation outbreak in USRW that began in 2006, peaked in 2007, and wound down in 2008 and 2009 (Townsend et al., 2012; Cowles et al., 2014). Previous studies conducted in the Appalachians have shown that such defoliation outbreaks can produce transient spikes in surface water NO_3^- concentrations and yields that can continue for several years following the initial wave of disturbance (Eshleman et al., 1998). We used disturbance index (DI) metrics for 2007 for the 23 predominantly-forested watersheds in USRW to test whether watershed-scale defoliation affected long-term NO_3^- concentration trends; DI metrics were previously generated by Cowles et al. (2014) for USRW using the method of Healey et al. (2005). Synoptic stations with watersheds that had been highly disturbed in 2007 (i.e., $\text{DI} > 1$) typically had NO_3^- trends that were somewhat less certain than those with lesser disturbance (i.e., $\text{DI} < 0$); this is illustrated by wider error bars on the trends

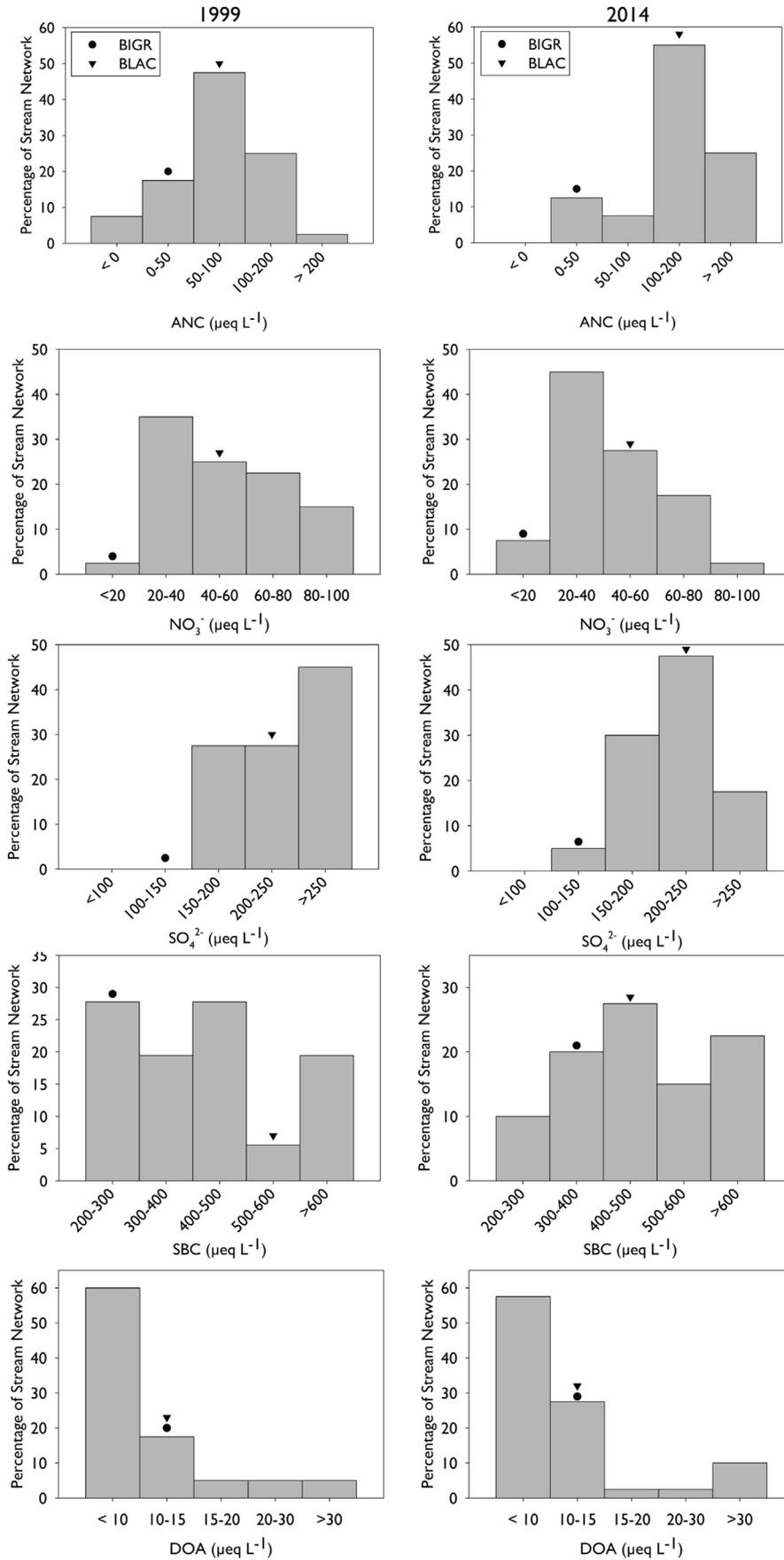


Fig. 4. Frequency distributions for major acid-base constituents measured during the spring 1999 and 2014 baseflow surveys conducted in USRW. Annual discharge-weighted mean concentrations for BGR and BLAC for the same water years are also shown for visual comparison.

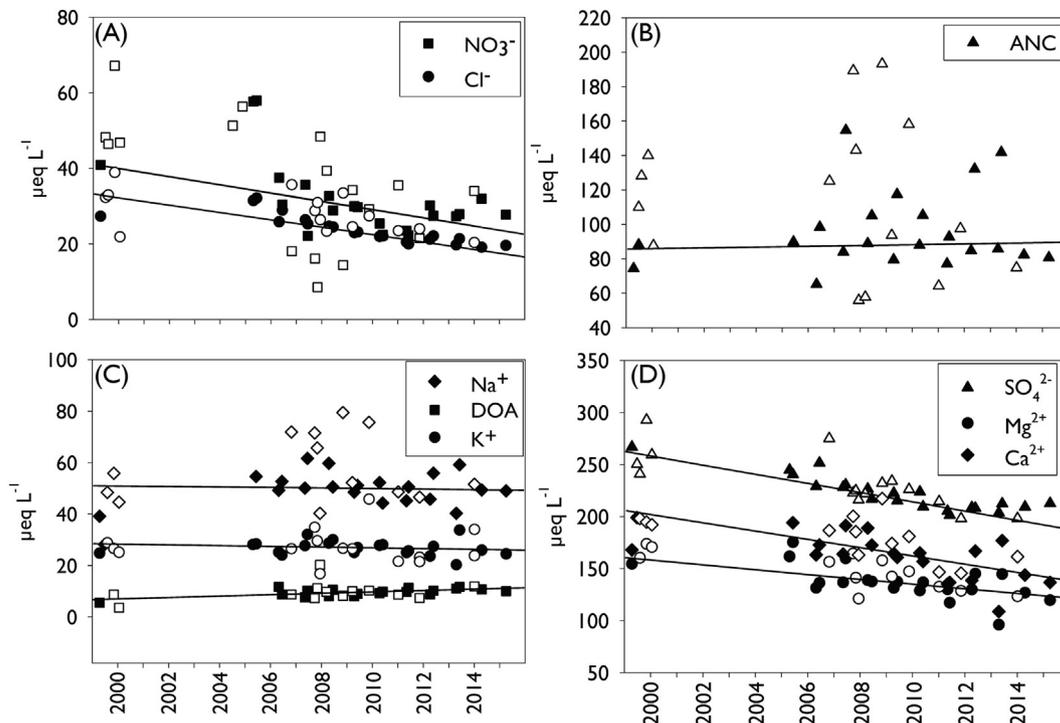


Fig. 5. Time series of raw (A) NO_3^- and Cl^- concentrations; (B) ANC; (C) Na^+ , DOA, and K^+ concentrations; and (D) SO_4^{2-} , Mg^{2+} , and Ca^{2+} concentrations measured at site BBL112 during the study. MKT lines based only on samples collected under spring baseflow conditions (closed symbols) are shown. Open symbols include all samples collected during other seasons or under stormflow conditions that were not used for trend analysis.

(Fig. 7). These results also suggest that the magnitude of the NO_3^- concentration trend may be slightly less negative (or even positive) for the most highly disturbed systems compared to those that were minimally disturbed—similar to results obtained by Eshleman et al. (2009). Our results thus explain to some extent why the range in NO_3^- concentration trends based on the 40 synoptic stations may be so large.

We also observed significant decreasing Ca^{2+} , Mg^{2+} , and K^+ concentration trends in the synoptic results for a total decline of about $3.6 \mu\text{eq L}^{-1} \text{yr}^{-1}$; this is about $1 \mu\text{eq L}^{-1} \text{yr}^{-1}$ greater than the regional decline in acid anion (NO_3^- and SO_4^{2-}) concentrations. Including the increasing trend in Na^+ concentration effectively zeros out any long-term regional trend in ANC (Table 2). The lack of a regional recovery trend in ANC can thus be explained by the fact

Table 1
Summary of the results from the station homogeneity and trend tests for the 40 USRW surface water stations and the three central Appalachian regional NADP wet deposition stations.

Constituent	USRW χ^2 Values		Regional NADP χ^2 Values	
	Homogeneity	Trend	Homogeneity	Trend
ANC/Inferred ANC	25.7 ^a	3.60	0.15 ^a	48.64 ^b
Cl^-	251	NH	3.34 ^a	14.83 ^b
NO_3^-	61.2 ^a	83.6 ^b	0.04 ^a	44.7 ^b
SO_4^{2-}	65.5 ^a	130 ^b	0.26 ^a	34.6 ^b
Na^+	38.7 ^a	71.3 ^b	6.15	
K^+	27.7 ^a	98.0 ^b	0.32 ^a	0.15
Mg^{2+}	42.3 ^a	60.7 ^b	1.06 ^a	2.78
Ca^{2+}	45.1 ^a	90.4 ^b	4.16 ^a	0.19
NH_4^+	NA	NA	2.67 ^a	0.01
DOA	30.7 ^a	13.9 ^b	NA	NA

NH = not homogeneous.

NA = data not available.

^a Indicates homogeneity of trend direction, $p \leq 0.001$.

^b Indicates statistically significant trend over time, $p \leq 0.001$.

that the regional decreasing trends in both NO_3^- and SO_4^{2-} (and increasing trend in Na^+) are almost exactly counterbalanced by decreasing trends in Ca^{2+} , Mg^{2+} , and K^+ concentrations. Although Cl^- did not show a significant regional trend, it is interesting to note that some individual stations demonstrated significant increasing trends for Cl^- (and Na^+) concentration which we believe can most likely be attributed to increasing application of road deicing salts across the USRW (Kaushal et al., 2005).

In contrast to trend results for other regions (Evans et al., 2005; Monteith et al., 2007; Erlandsson et al., 2011), none of our data suggest much of a role for DOA in the ANC recovery process given the lack of a statistically significant trend for DOA with RKT. Only three individual sites, exhibited statistically significant positive trends for DOA, suggesting that although not a factor at the scale of the entire basin, DOA trends could actually be hampering ANC recovery of selected streams (Driscoll et al., 2003; Evans et al., 2008; Erlandsson et al., 2011).

No basin-wide statistically significant trend in ANC was observed (Table 2), despite the fact that declines in NO_3^- and SO_4^{2-} surface water concentrations were observed across the basin—likely driven by declining atmospheric S and N deposition as discussed. Four of the 40 individual stations demonstrated a significant ($p \leq 0.05$) trend, however, and all four trends were positive (Table S10). Examining the distribution of mean spring baseflow ANC across the stream network, we found that 10% of the network is characterized by mean ANC $< 50 \mu\text{eq L}^{-1}$, 12.5% by mean ANC between 50 and $100 \mu\text{eq L}^{-1}$, 50% by mean ANC between 100 and $200 \mu\text{eq L}^{-1}$, and 27.5% by mean ANC greater than or equal to $200 \mu\text{eq L}^{-1}$. Of these classes, the lowest ANC class showed a disproportionately high percentage (75%) of reaches showing statistically significant (positive, $p \leq 0.05$) trends in ANC during the study; 75% of the reaches showing a significant trend had a mean ANC $< 50 \mu\text{eq L}^{-1}$, with the other 25% contained in the 100– $200 \mu\text{eq L}^{-1}$ class (Fig. 8). The mean trend in ANC based on

Table 2

Results from RKT analysis for surface water and wet deposition constituents passing χ^2 tests for homogeneity and trend with calculated Sen slope values and lower (LCL) and upper (UCL) 95% confidence limits.

Constituent	USRW RKT			Regional NADP RKT		
	Sen slope ($\mu\text{eq L}^{-1} \text{yr}^{-1}$)	LCL	UCL	Sen slope ($\mu\text{eq L}^{-1} \text{yr}^{-1}$)	LCL	UCL
ANC/Inferred ANC ^b	NS	—	—	2.6 ^a	3.0	2.2
Cl ⁻	NS	—	—	-0.06 ^a	-0.08	-0.03
NO ₃ ⁻	-0.82 ^a	-1.0	-0.63	-0.92 ^a	-1.07	-0.71
SO ₄ ⁻	-1.5 ^a	-1.9	-1.3	-2.1 ^a	-2.4	-1.7
Na ⁺	1.1 ^a	0.77	1.4	NS	—	—
K ⁺	-0.29 ^a	-0.36	-0.22	NS	—	—
Mg ²⁺	-0.81 ^a	-1.1	-0.55	NS	—	—
Ca ²⁺	-2.5 ^a	-3.20	-1.7	NS	—	—
NH ₄ ⁺	NA	—	—	NS	—	—
DOA	0.05	-0.00	0.10	NA	—	—

^a Statistically significant ($p \leq 0.05$).

^b Calculated from H⁺; NS = not statistically significant; NA = not available.

these four stations was $2.0 \mu\text{eq L}^{-1} \text{yr}^{-1}$ —nearly identical to the values for extremely acid-sensitive BIGR shown in Fig. 3. We must thus conclude that BIGR appears to be representative of the group of extremely acid-sensitive USRW watersheds that is showing evidence of significant ANC recovery.

Relaxing the p value (first to 0.25 and finally to 0.33) essentially doubles the percentage of reaches showing significant trends in ANC during the 15-year study period; at the 0.33 p level, 20% of the reach network showed a statistically significant trend and the trends were universally increasing; the mean trend at this p level

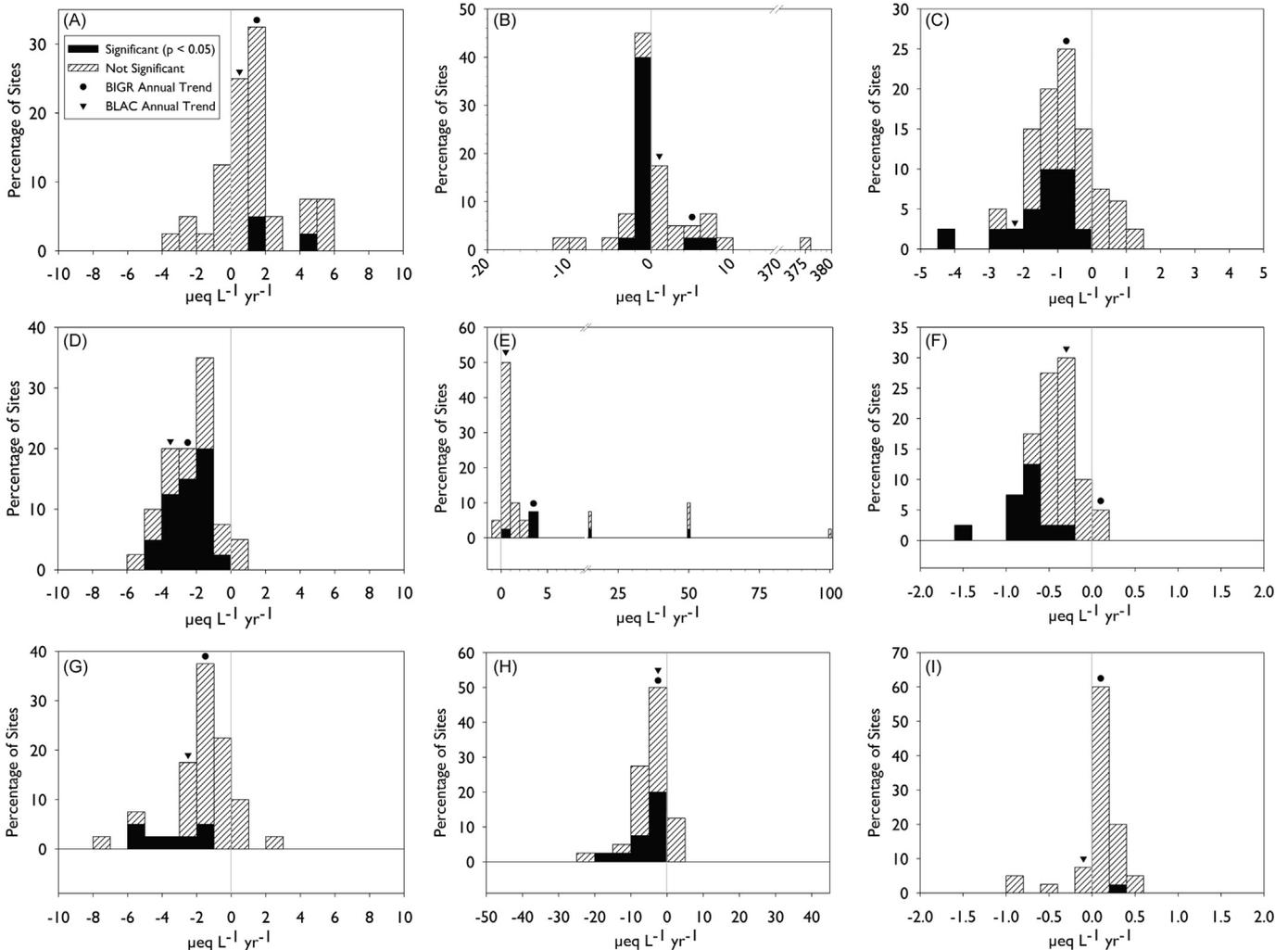


Fig. 6. Frequency distributions of annual trends ($\mu\text{eq L}^{-1} \text{yr}^{-1}$) for (A) ANC, (B) Cl⁻, (C) NO₃⁻, (D) SO₄²⁻, (E) Na⁺, (F) K⁺, (G) Mg²⁺, (H) Ca²⁺, and (I) DOA based on MKT analysis; trends for BIGR and BLAC are also shown.

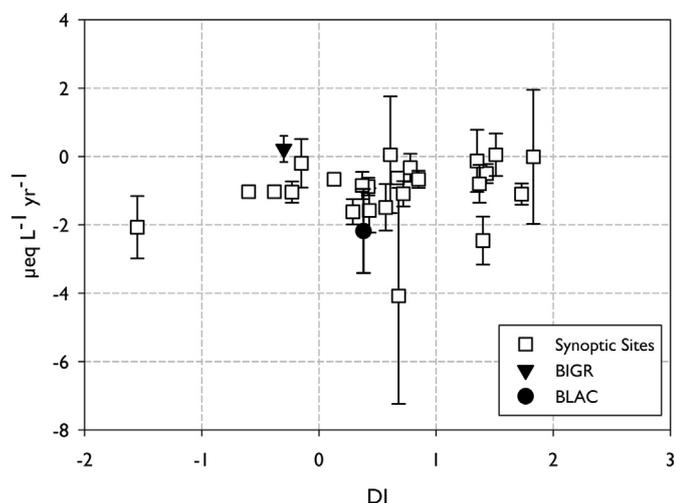


Fig. 7. MKT NO_3^- trends (with 95% confidence intervals) for 23 predominantly-forested (>75% forest cover) watersheds, BIGR, and BLAC vs. Disturbance Index (DI) in 2007.

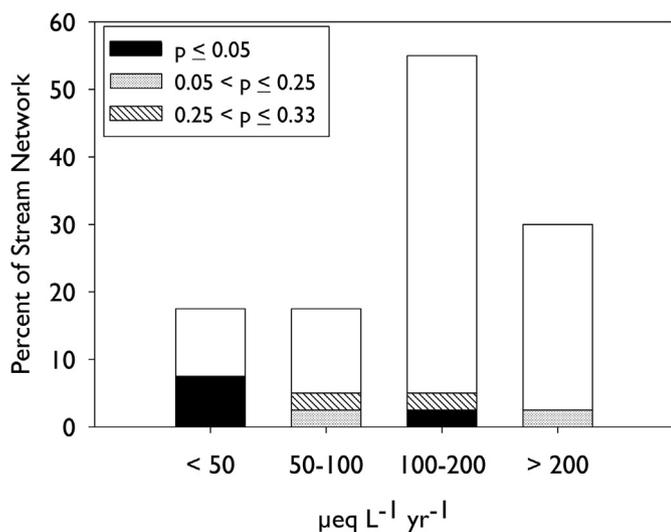


Fig. 8. Frequency distribution of mean ANC in USRW during the study period, with the percentages of stream reaches showing statistically significant ANC trends based on MKT at three different p levels.

only increased slightly to $2.5 \mu\text{eq L}^{-1} \text{yr}^{-1}$. The additional reaches showing significant trends are found mostly in the 50–100 $\mu\text{eq L}^{-1}$ ANC class (Fig. 8), but this computation does not affect our conclusion that some significant ANC recovery appears to be occurring especially in the most acid-sensitive streams in the USRW. It seems likely that monotonic ANC recovery is occurring across the basin, but the “signal” is simply too small to distinguish from the “noise” attributable to natural variability at most of the synoptic stations. In the most acid-sensitive stations (i.e., $\text{ANC} < 50 \mu\text{eq L}^{-1}$), however, the noise was sufficiently small, thus allowing us to identify and quantify an ANC recovery signal (i.e., a trend). Extrapolating data from BIGR to the entire USRW suggests that ANC recovery likely began at least as early as 1990—initially in response to declining SO_4^{2-} deposition brought on by SO_2 emission controls under the CAAA (Eshleman et al., 2008), and later (mid 1990s) as regional NO_x controls were implemented primarily to meet atmospheric ozone standards (Eshleman et al., 2013; Eshleman and Sabo this issue).

4. Conclusions

- Mid-to late-spring timing of sampling under baseflow conditions (after snowmelt but before leaf out) maximized our ability to predict annual average acid-base conditions across the USRW using synoptic survey data.
- Decreasing trends in surface water NO_3^- and SO_4^{2-} are nearly ubiquitous across USRW, reflecting dramatic declines in atmospheric deposition owing to SO_2 and NO_x emission controls under CAAA and other regulatory programs.
- Significant ANC recovery was observed in 10–20% of USRW stream reaches (depending on the p level used), but the magnitude of the trend relative to natural variability was apparently insufficient to allow detection of a basin-wide ANC trend.
- Decreasing trends in K^+ , Mg^{2+} , and Ca^{2+} concentrations exceeded decreasing trends in NO_3^- and SO_4^{2-} concentrations by about $1 \mu\text{eq L}^{-1} \text{yr}^{-1}$, moderating any regional recovery in ANC.
- DOA has not played a major role in the ANC recovery process in USRW.
- RKT appears to be a robust method for identifying basin-wide trends using synoptic data, but MKT results for individual systems should be examined closely (e.g., to identify trends for specific subpopulations).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2016.07.034>.

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