

FLOW-SPECIFIC TRENDS IN RIVER-WATER QUALITY RESULTING FROM THE EFFECTS OF THE CLEAN AIR ACT IN THREE MESOSCALE, FORESTED RIVER BASINS IN THE NORTHEASTERN UNITED STATES THROUGH 2002

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Abstract. Two new methods for assessing temporal trends in stream-solute concentrations at specific streamflow ranges were applied to long (40 to 50-year) but sparse (bi-weekly to quarterly sampling) stream-water quality data collected at three forested mesoscale basins along an atmospheric deposition gradient in the northeastern United States (one in north-central Pennsylvania, one in southeastern New York, and one in eastern Maine). The three data sets span the period since the implementation of the Clean Air Act in 1970 and its subsequent amendments.

Declining sulfate (SO_4^{2-}) trends since the mid 1960s were identified for all 3 rivers by one or more of the 4 methods of trend detection used. Flow-specific trends were assessed by segmenting the data sets into 3-year and 6-year blocks, then determining concentration-discharge relationships for each block. Declining sulfate (SO_4^{2-}) trends at median flow were similar to trends determined using a Seasonal Kendall Tau test and Sen slope estimator. The trend of declining SO_4^{2-} concentrations differed at high, median and low flow since the mid 1980s at YWC and NR, and at high and low flow at WR, but the trends leveled or reversed at high flow from 1999 through 2002. Trends for the period of record at high flows were similar to medium- and low-flow trends for $\text{Ca}^{2+} + \text{Mg}^{2+}$ concentrations at WR, non-significant at YWC, and were more negative at low flow than at high flow at NR; trends in nitrate (NO_3^-), and alkalinity (ALK) concentrations were different at different flow conditions, and in ways that are consistent with the hydrology and deposition history at each watershed. Quarterly sampling is adequate for assessing average-flow trends in the chemical parameters assessed over long time periods (~decades). However, with even a modest effort at sampling a range of flow conditions within each year, trends at specified flows for constituents with strong concentration-discharge relationships can be evaluated and may allow early detection of ecosystem response to climate change and pollution management strategies.

Keywords: river water-quality trends, acid rain, trends methods, northeastern US

1. Introduction

Acidic deposition (“acid rain”) continues to adversely affect terrestrial and aquatic ecosystems in the eastern United States (Driscoll *et al.*, 2001). However, rates of nitrate (NO_3^-) deposition stabilized during the 1990’s, rates of sulfate (SO_4^{2-}) deposition declined (Likens *et al.*, 1996; Driscoll *et al.*, 2001), and some recovery of alkalinity (ALK) is taking place in surface waters of the Northeast (Stoddard *et al.*, 2003; Burns *et al.*, 2005). Estimates of this recovery are based on both

non-parametric and regression-based trends analyses that utilize either periodic sampling (1 sample per month or season), or assume that the samples are randomly distributed over both time and flow condition (Stoddard *et al.*, 2003; Burns *et al.*, 2005). Flow-adjusted trend analysis (the effect of flow was removed from the trend) was used in some cases to account for the variation in stream discharge between sampling times, and to thus eliminate the effect of flow as a factor in the observed trend (Hirsch *et al.*, 1982). The methods currently used for trend detection therefore provide estimates of water quality change integrated across all flow conditions.

A drawback of current methods of trend detection is the lack of accounting for episodic changes in surface-water chemistry associated with rainstorms and snowmelt. If the goal is to track the effects of chemical constituents such as SO_4^{2-} or NO_3^- that are deposited on the surface of a watershed, our understanding of hydrology suggests that changes in deposition should be reflected in streams during high-flow conditions before changes are detected at low flow. Soils and streams become acidified by deposition through a multistep process that has been described by Aber *et al.* (1989) and Stoddard (1994), respectively. The Stoddard conceptual model indicates that stream acidification will initially be manifested during stormflows, when acids that have entered shallow soil horizons are flushed into streams. Chronic stream acidification results from the gradual extension of acidic episodes into the baseflow periods through the infiltration of acidic soil water to the groundwater system that sustains baseflow. Accordingly, the decrease in the acidity of precipitation that has been documented since the early 1990s would be expected to result in a decrease in the acidity of water in shallow flowpaths, and thus in stormflows, earlier than in deeper ground water and baseflow. Assessment of the early effects of emission reductions on stream-water quality would therefore require sufficient stormflow sampling to assess whether solute concentrations in stormflows are changing through time.

A comparison of NO_3^- concentrations in samples collected during the 1940's and the 1980's in a river in the Catskill Mountains of New York shows that the average NO_3^- concentration did not change over time nearly as much as the peak concentrations during snowmelt and rainstorms (Stoddard and Murdoch, 1991). Further, bioassay experiments in which brook trout were held in cages in Catskill streams showed that pH and aluminum concentrations that were toxic to fish occurred during short-duration pulses referred to as "episodic acidification" (Van Sickle *et al.*, 1996). If the biologically-relevant changes in surface-water chemistry occur during these events, then tracking the recovery from acid deposition should include some sense of whether episodic acidification is diminishing. Subtle trends in water quality, such as trends that are occurring at high flows but not at low flows, cannot be detected by current statistical methods used in trend analysis. Several factors, including local physiography, soil chemistry and transmissivity, and precipitation rates and distribution affect a basin's response to changes in SO_4^{2-} and NO_3^- deposition. Long-term trends in stream-water quality are difficult to separate from the "noise" of local conditions. Assessments of trends in the storm flows of rivers

have been made (Baldigo, 1999; Hodgkins *et al.*, 2003; Lins and Slack, 1999), but assessments of trends in water quality at high- versus low-flow conditions have not been attempted to date.

The Clean Air Act (CAA) of 1970, as amended in 1977 and 1990, represented a national scale experiment in pollution abatement in the United States (Driscoll *et al.*, 2001). The CAA amendments of 1990 mandated large reductions in the emission of sulfur and nitrogen compounds from industrial and power-generating plants over a 20-year period, with the assumption that these reductions would decrease the acidity of rainfall in areas downwind of the plants and thus reduce the acidification of waters and soils in those regions. Assessing whether these expensive mitigation steps will yield the anticipated results requires monitoring of environmental parameters before, during, and after the changes are implemented. Most research on the effects of acid rain has been carried out in small, high-relief watersheds (i.e., areas of several hectares to a few square kilometers), and little monitoring has occurred in non-developed, larger river basins more typical of the landscapes in which people live and are actively altering ecosystems. Indeed, there are few locations in the United States where non-developed, meso-scale (25–650 km²) watersheds can be monitored as a reference for understanding the changes in water quality occurring in developed landscapes. There are some meso-scale rivers draining minimally-developed watersheds in northern Europe that have been monitored for continuous discharge and at least monthly water quality since the early 1980s (Kristensen and Brand, 1996), and in a few cases there are records since the 1960s, but determining trends in water quality at high flow in these rivers has not been attempted. In this paper we analyze trends in water quality in three such meso-scale basins in the northeastern USA, using new methods to assess how trends may differ at different flow regimes.

1.1. THE STUDY AREA

The U.S. Geological Survey (USGS) Hydrologic Benchmark Network (HBN) was established in the early 1960's to provide a set of indicator measurements of water quality in undisturbed landscapes that could serve as a baseline or "benchmark" for assessing the effect of human activities on river-water quality (Mast and Turk, 1999). The focus of the HBN is on rivers draining "mesoscale" basins—those with areas ranging from 25 to 650 km² and with hydrologically-significant riparian zones and flood plains—to provide a long-term database of water quality in undisturbed basins similar to those that are being rapidly altered by humans. The HBN is the world's only network of undeveloped mesoscale watersheds that has been systematically monitored over time, and has been the basis of several assessments of water-quality trends (Smith and Alexander, 1983; Clow and Mast, 1999; Lewis, 2002; others). Water-quality sampling was terminated in 1997 at all but five of the stations, three of which are in the Northeastern US (Figure 1); these three sites were maintained to track the effects of industrial-emission reductions mandated by the CAAA.

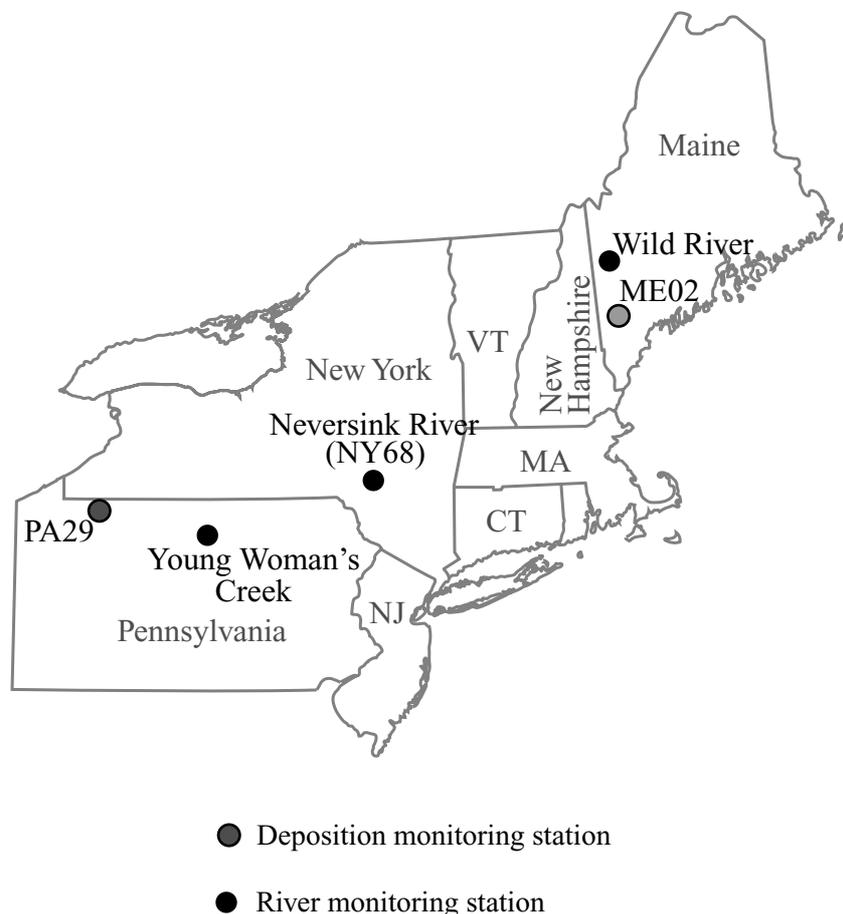


Figure 1. Map of Northeastern US showing the location of HBN river monitoring stations and NTN deposition monitoring stations used in this study. Deposition station within the Neversink watershed is designated in parentheses.

The three HBN river monitoring stations used in this study (Figure 1 and Table I) are Young Woman's Creek (YWC; 38 years of record) near Renovo, Pennsylvania, the Wild River (WR; 35 years of record) near Gilead, Maine, and Neversink River (NR; 50 years of record) near Claryville, New York. The YWC and WR stations have been maintained by the HBN program since their inception; NR has been monitored continuously by the USGS for discharge, intermittently for water quality by the New York City Department of Environmental Protection (NYCDEP) and the USGS since 1952, and biweekly and during high-flow conditions by the USGS since April 1991. The NR was designated as an HBN station in April 1997.

The three monitoring stations lie along a sulfur- and nitrogen-deposition gradient that extends from central Pennsylvania to eastern Maine (Table II). The highest deposition rates of hydrogen (H^+), SO_4^{2-} , and NO_3^- are at the southwestern end of the

TABLE I

Physical features of the three study watersheds in north-central Pennsylvania, southeastern New York and western Maine (locations are shown in Figure 1)

Characteristic	Young Woman's Creek, PA	Neversink River NY	Wild River ME
Gage latitude	41°23'22'	41°53'24'	44°23'27'
Gage longitude	77°41'28'	74°35'25'	70°58'47'
Gage elevation (meters above sea level)	238	480	208
Relief (m)	427	800	1270
Drainage area (km ²)	120	166	180
Mean precipitation (cm/yr)	105	175	119
Period of record	1964–2002	1952–2002	1967–2002

TABLE II

Five-year mean annual deposition and concentrations of selected constituents at three NTN stations in Pennsylvania (PA29), New York (NY68), and Maine (ME02), water years^a 1997–2002

State	Deposition (cm)	Concentration ($\mu\text{eq/L}$)				Specific conductance ($\mu\text{S/cm}$)
		H ⁺	NO ₃ ⁻	SO ₄ ²⁺	Ca ²⁺ + Mg ²⁺	
Pennsylvania	105.2	51.3	28.0	47.7	7.27	27.5
New York	136.8	36.8	21.0	31.4	4.15	19.7
Maine	107.1	25.0	14.9	14.9	3.85	14.3

^aWater year is 12-month period from October 1 through September 30 of following year.

study gradient, and lowest rates are in the northeast. SO₄²⁻ and NO₃⁻ concentrations in river water also are greatest in the southwest (YWC) and lowest in the Northeast (WR), but YWC also had the highest ALK because of greater availability of base cations within the YWC watershed (Table III). All three basins are nearly 100%

TABLE III

Five-year mean annual river water concentrations of selected constituents in Pennsylvania, New York, and Maine, water years^a 1997–2002

State	Discharge (cms/yr ⁻¹)	Concentration ($\mu\text{eq/L}$)				Alkalinity ($\mu\text{eq/L}$)
		pH	NO ₃ ⁻	SO ₄ ²⁻	Ca ²⁺ + Mg ²⁺	
Pennsylvania (YWC)	2.08	6.9	20.0	170	282	180
New York (NR)	5.32	6.5	13.4	106	183	83
Maine (WR)	5.29	6.4	7.1	99	116	98

^aWater year is 12-month period from October 1 through September 30 of following year.

forested with mixed hardwood; spruce and fir are found along the ridge tops in the NR basin and are distributed more widely in the WR basin in Maine. Soils in the WR basin are acidic spodosols; soils in the NR and YWC basins are acidic inceptisols (Mast and Turk, 1999). Soils in NR and WR are developed on till, and those in the YWC basin are developed on bedrock. Bedrock at YWC is sandstone, shale, and siltstone; bedrock at NR is sandstone, shale, and conglomerate; and bedrock at WR is gneiss, mica schist, and quartzite (Clow and Mast, 1999). Aside from atmospheric deposition, human effects on water quality are minimal in all three basins. The WR basin primarily drains National Forest land and contains one paved road in its lower watershed and one unpaved road that provides seasonal access to the upper basin. Logging within this basin has resulted in the thinning of 3,600 ha of forest (20% of basin area) over the past 35 years (Mast and Turk, 1999). The headwaters of NR are owned by the State of New York and are designated "forever wild." The valley bottoms are privately owned and contain summer homes, fishing camps, and a YMCA environmental education center. A small village lies near the junction of the east and west branches of the Neversink River upstream of the HBN monitoring station. Road salt may affect river-water quality during the spring. Most of the YWC basin drains State Forest land, and is undeveloped except for a few small dwellings in the lower reaches. The drainage divides are high plateaus where minor clearing and development has occurred within the drainage area. Gravel roads that are not maintained during the winter parallel each of the two branches of the Creek and transect the basin from its mouth to the ridgetop. Limestone gravel may have been added to parts of this road during maintenance. Detailed descriptions of the three basins are given in Mast and Turk (1999; YWC and WR) and Lawrence *et al.* (2001; NR).

2. Approach

Recently-developed methods of trend detection at high, medium, and low flow conditions (Murdoch and Shanley, in press) were applied to the data sets from the three HBN basins. Quarterly to monthly water quality records prior to 1997, herein referred to as the historical record, were appended with a 5-year record based on more frequent sampling from 1997 through 2002. The principal objective of the study was to apply newly developed methods of flow-specific trend detection to the three sparse data sets to (a) define water-quality trends during high-, medium-, and low-flow conditions, and (b) determine if high-flow trend analysis could provide a more sensitive test for trend detection in sparse data sets. A second objective of the study was to (1) determine the optimum sampling frequency for monitoring the response of the three selected rivers to changes in deposition chemistry; and (2) document the initial effects of the CAAA on river-water quality in the northeastern United States.

2.1. METHOD OF SAMPLING AND SAMPLE ANALYSIS

2.1.1. *Collection and Analysis of River-Water Samples*

The HBN data set for YWC and WR consists of 15-minute interval discharge data and monthly to quarterly water-quality data beginning in October 1967. The HBN water-quality sampling program was terminated in September, 1996 at YWC and WR, but was re-started at these stations in April, 1997, and has supported both biweekly and stormflow sampling since. NR discharge was monitored by the USGS, and water sampling was done by the New York City Department of Environmental Protection (NYCDEP) at Claryville, N.Y., from 1952 to present. The NR monitoring station has been sampled biweekly and during stormflows by the USGS since 1991.

All samples collected at YWC and WR before April 1997 were obtained manually using depth-integrated sampling techniques (USGS, 1999). Samples were collected manually from 1952–1991 at NR, and both manually and by automated sampler since. The three study sites have been equipped since April 1997 with continuous water-temperature sensors and automated water samplers that were programmed to collect samples during stormflows and snowmelt periods. Quarterly, depth-integrated, equal-area samples and manually-collected streamside samples were collected concurrently with automated samples during the first 2 years of the study to test the comparability of automated, depth-integrated, and manual methods of sampling. These samples were split for analysis at the Troy USGS laboratory in Troy, NY, and the USGS National Water Quality Laboratory (NWQL) in Colorado, where the HBN samples had been analyzed prior to 1997. Samples collected by the automated sampler were retrieved either within 48 hours of sample collection or within 4 days if samplers were refrigerated at the monitoring station, and shipped chilled overnight to the Troy laboratory for processing and analysis.

Samples collected in 1997 and thereafter were analyzed at the Troy laboratory for 16 constituents. Of these, calcium (Ca), magnesium (Mg), SO_4^{2-} , NO_3^- , and ALK are considered in this study. Samples from YWC and WR before 1997 were filtered in the field and analyzed for these constituents and others at the NWQL. Samples from NR were not analyzed for SO_4^{2-} until 1991. Laboratory methods for samples from NR, and from all three sites after 1996, are documented in Lawrence *et al.* (1995, 2001). Laboratory methods used before 1997 for samples from the three sites are documented in Fishman and Friedman (1989). The subset of samples analyzed by both the Troy laboratory and the NWQL indicated no significant bias derived from the change in primary laboratory for the constituents assessed in this study (G. Lawrence, USGS, written communication, 2002).

2.1.2. *Quality Assurance and Quality Control for River-Water Samples*

The paired results from integrated sampling over the stream cross-section and automated sampling from a fixed point showed no significant difference, thus the results could be pooled in a common long-term data set for trend analysis (G. Lawrence, U.S. Geological Survey, written commun., 2001). Further, analyses of sample splits

sent to both laboratories providing water analyses for this study, the Troy research laboratory and the USGS NWQL, were comparable and indicated no analytical bias based on standard quality assurance tests. Results of the NWQL's participation in laboratory performance evaluations are presented at <http://nwql.cr.usgs.gov>, and those for the Troy laboratory are published periodically (Lincoln *et al.*, 1996, 2004). One set of triplicate samples was collected in the field for every 50 samples for this study. The data from samples collected by the 2 methods and processed by the two laboratories were therefore combined into a common database for statistical analysis.

Two additional data adjustments were done to make the historical and recent data sets comparable. Acid-neutralizing capacity (ANC) values calculated by Gran titration (Gran, 1952) for samples collected after October 1997 were recomputed from the original titration data to a fixed-endpoint of pH 4.5 for direct comparison to ALK values in the historical record. For the entire data set and from all 3 sites, ANC averaged $35.5 \mu\text{eq/L} \pm 0.01$ less than ALK ($F^2 = .99$, $p < .0001$). Data quality for the HBN network before 1997 was analyzed by Mast and Turk (1999). Bias in SO_4^{2-} analyses within the HBN program during the 1980s resulted in the censoring of some SO_4^{2-} data during that period (Clow and Mast, 1999). The present study used only the uncensored values.

2.1.3. Collection and Analysis of Atmospheric Deposition Samples

Precipitation volume and chemistry were used from the National Trends Network (NTN) stations nearest to each HBN station (Figure 1). Weekly composite samples were collected on Tuesday at each of the 3 stations and were shipped to the Central Analytical Laboratory in Champaign, Ill., for processing and analysis. Precipitation amount was measured at each site with a weighing-bucket gage. Field methods and laboratory procedures, quality-assurance and quality-control procedures, and results for the NADP program are reported at <http://nadp.sws.uiuc.edu>. NADP data analyzed in this paper include precipitation amount, pH, and concentrations of SO_4^{2-} , NO_3^- , and base cations.

2.2. TREND ANALYSIS

Water quality trends for the period of record were determined by 4 methods described below, including 2 established methods for trend detection in the entire record, and 2 newly developed methods for trend detection at specific flow regimes. The 2 standard methods are the non-parametric, flow-adjusted Seasonal Kendall's Tau (Helsel and Hirsch, 1992), and the parametric Multiple Regression Residuals Analysis (MRRA) (Aulenbach and Hooper, in press; Murdoch and Shanley, in press). Results from the standard methods serve as a benchmark from which to evaluate results from the new methods. In addition, an Analysis of Covariance (ANCOVA) was applied to test for differences in slope of the concentration-discharge (C-Q) relations in successive time periods, as would be expected if trends dif-

fer at different flows. The two flow-specific trends tests presented here are the Segmented Regression Analysis (SRA; Murdoch and Shanley, in press), which determines trends by computing C-Q relations for sequential temporal segments, and a MRRA by flow class (FC-MRRA), in which trends are computed from residuals of concentration models developed for discrete flow classes. Brief descriptions of each method are presented below:

2.2.1. *Seasonal Kendall's Tau (SKT) Analysis*

The SKT is a non-parametric test that compares flow-adjusted concentrations in specific seasons (or shorter interval, such as months), then averages the seasonal trends to define a long-term trend for each constituent. The SKT test does not require linearity of trends or normality of the data, and is not sensitive to outliers or missing values (Helsel and Hirsch, 1992). A flow-adjusted SKT statistic (Helsel and Hirsch, 1992) was computed to analyze trends in solute concentrations in river water at the 3 HBN sites and in precipitation at the 3 associated NADP stations. The sample that was collected closest to the midpoint of each season was used for this analysis. Rates of change in concentration were calculated by the SEN slope estimator, which defines the direction and rate of change as the median of the slopes among the set of seasonal pair-wise comparisons (e.g. October 1991 vs October 1992, etc.; Clow and Mast, 1999). Trends using volume-adjusted SKT were assessed for 2 periods of time: the entire period of record which differed for each river, and a period common to all precipitation and river monitoring data sets (1984–2002 at YWC and WR, and 1991–2002 at NR). In addition, trends were determined for the 1984–1996 period previously analyzed for deposition trends by Clow and Mast (1999), and which includes the 1995 period of rapid reduction in SO_4^{2-} emissions. Differences in trends among these three periods were used as an indicator of changes in trends over time.

2.2.2. *Multiple Regression Residual Analysis (MRRA)*

Trends in solute concentrations were evaluated from the residuals of multiple regression concentration models (Aulenbach and Hooper, in press; Huntington *et al.*, 1994). The model for each solute ($\text{Ca}^{2+} + \text{Mg}^{2+}$, ALK, NO_3^- , and SO_4^{2-}) at each site incorporated a discharge term and a seasonal term. The discharge term, defined by the Johnson flow model (Johnson, 1969), had the form $1/(1 + \beta Q_a)$, where β is a constant, Q is river discharge, and a is an antecedent period over which discharge was averaged. For each sample, Q_a was calculated for $a = 0, 1, 6,$ and 12 hours and $1, 2, 5, 10, 20, 30, 45, 60,$ and 90 days. Each model was optimized for a and β . The seasonal terms were sine, cosine, sine/2, and cosine/2 of the day of year, in radians. The inclusion of sine and cosine terms allowed for the optimization of the amplitude and phase of each seasonal trend; the half-sine and half-cosine terms accounted for shorter-term variability. Only the instantaneous-sample discharges for YWC and WR were available before 1997; thus, the discharge terms in the models, including the pre-1997 period for these two sites, were limited to $a = 0$. The

models constructed for each site were based on either the full data set or a subset of quarterly data. Residuals of the models were analyzed for temporal trends through linear regression. Time was purposely excluded from the models as a variable so that temporal trends would appear in the model residuals.

2.2.3. *Multiple Regression Residual Analysis by Flow Class (FC-MRRA)*

If samples collected within a specific flow class are well distributed throughout the period of record, the MRRA trend analysis can be performed on that flow class. The sparse sampling at the three HBN sites necessitated rather broad flow classes; >80% flow duration for low flow and <20% flow duration for high flow. A subset of quarterly samples from the recent (1997–2002) data was used to avoid biasing the model with the disproportionately large number of samples from this period.

2.2.4. *Segmented Regression Analysis (SRA)*

Segmented regression analysis (SRA) uses C-Q relations determined for discrete temporal segments of the data to calculate a concentration at a specific discharge for each segment, then compares those concentrations for trend (Murdoch and Shanley, in press). C-Q regressions were performed for each time segment for four constituents ($\text{Ca}^{2+} + \text{Mg}^{2+}$, ALK, NO_3^- , and SO_4^{2-}). The HBN data set was segmented into 6-year and 3-year segments, and each C-Q relation was tested for significance. The 6-year period of frequent sampling (1997–2002) was also split into 1-year segments to assess recent changes in C-Q relations at all three sites. The 15-minute discharge record for 1997–2002 was used to determine a 6-year average 5% (high flow), 50% (median flow), and 95% (low flow) duration flows for each site. No significant trends in discharge were observed by SKT analysis for the period of record at each of the rivers. Provided the C-Q relation was significant ($p < 0.05$) for each segment, concentrations for each constituent were calculated at each of these three discrete discharge values. If the C-Q relationship for a 3-year segment was not significant, the 6-year segment was used in place of the two 3-year segments it represented. If the C-Q relationship for that segment was also not significant, a gap was left for that period in the trend analysis. The resulting time series of concentrations for each flow range were analyzed for trends using linear regression. For comparison with trends determined by SKT, trends by SRA were determined for the same temporal segments.

2.2.5. *Analysis of Covariance (ANCOVA)*

The slope and intercepts of C-Q relations for each solute for two 6-year segments (1985–1990, 1991–1996) and two 3-year segments (1997–1999, 2000–2002) were compared through a four-way Analysis of Covariance (ANCOVA) test to discern whether the observed changes in concentration at specific flows over time were statistically significant (Helsel and Hirsch, 1992). The slope and y-intercept of the regression equations for each segment were tested for significant differences (Helsel and Hirsch, 1992).

3. Results

3.1. COMPARISON OF AVERAGE RIVER-WATER-QUALITY

Major ion concentrations differed in the 3 rivers in the study (Figure 2 and Table III). Flow-adjusted average concentrations of SO_4^{2-} , $\text{Ca}^{2+} + \text{Mg}^{2+}$, and ALK during the intensive sampling period of 1997–2002 were greatest at YWC and lowest at WR (Table III). Flow-adjusted average NO_3^- concentrations were similar at YWC and NR, and those at WR were generally below the reporting limit ($<2 \mu\text{eq/L}$) except for brief periods during snowmelt. The increased number of WR samples with NO_3^- concentrations above detection since 1997 is likely a result of the increased sampling frequency since April of that year. Average flow-adjusted ALK values were similar at WR and NR and much lower than at YWC; negative ALK concentrations (net acidity) at NR were common during spring snowmelt.

The LOWESS smoothing of the concentration timelines indicated differences in trends among the watersheds (Figure 2). SO_4^{2-} concentrations generally appear to have declined over the period of record in all of the rivers studied, but have

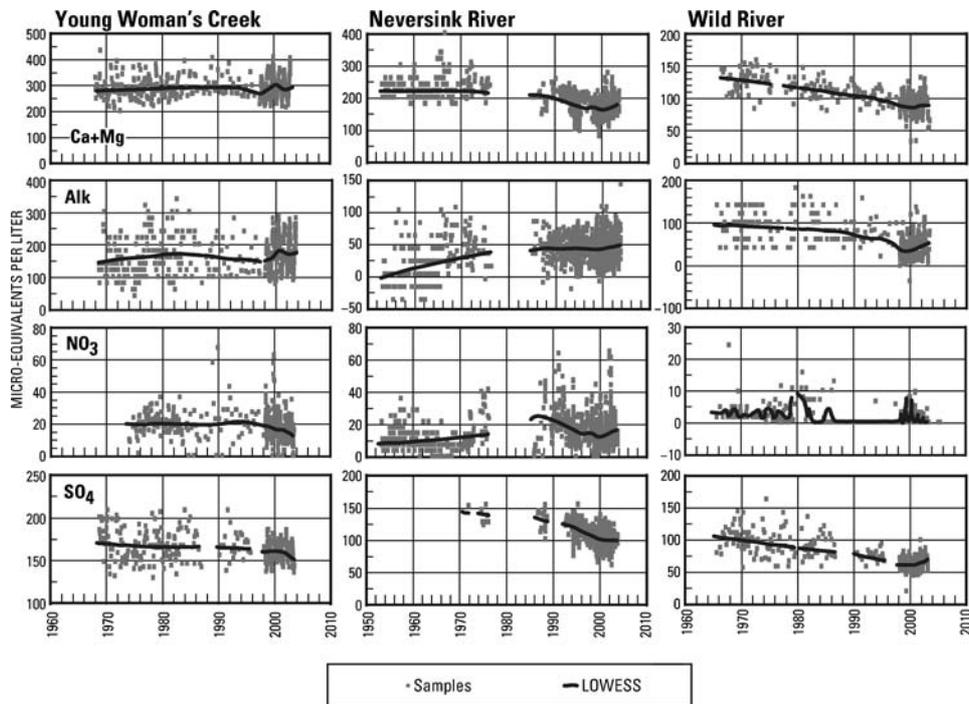


Figure 2. Timelines of SO_4^{2-} , NO_3^- , $\text{Ca}^{2+} + \text{Mg}^{2+}$, and ALK concentrations in samples collected from the 3 study rivers. A LOcally-WEighted Scatterplot Smoothing (LOWESS) line was applied to provide a smoothed image of visible trends (Helsel and Hirsch, 1992). The window for computation of the weighted, least-squares regression in each moving data segment was set at 0.5.

been relatively stable from 1997–2002 at NR and WR. NO_3^- concentrations were stable at YWC until a decline in the late 1990s, peaked in the late 1980s at NR, and were largely below detection except during spring melt at WR. $\text{Ca}^{2+} + \text{Mg}^{2+}$ concentrations changed little over the period of record at YWC, and declined until recently at NR and WR. ALK concentrations have been stable until a recent increase at YWC, and generally declined at WR until 1999, after which a slight increase is indicated. ALK at NR increased in the early years (1952–1976), stabilized through 2000, and may have started increasing since. These differences in the LOWESS curves among the 3 rivers indicate that differences in SKT, SRA, and MRRA trends should also be detectable.

3.2. TREND DETERMINATIONS

Assessments of 12 different trends (4 parameters at 3 rivers) were attempted by each of the four methods (Table IV). All trends based on the SKT and MRRA methods that are reported were significant to at least $p \leq 0.05$. A significance level of $p < 0.05$ for the C-Q relation in each individual segment in the SRA generally resulted in a sufficient number of statistically significant 3-year or 6-year data segments ($n > 9$) at each river to assess concentration trends at specific flow levels. SO_4^{2-} trends could not be calculated for NR before 1990 and for WR before 1996 due to insufficient sampling and/or laboratory bias. However, period of record trends in SO_4^{2-} determined using the flow-class MRRA were significant ($p < .01$) for the $<20\%$ (high flow) and $>80\%$ (low flow) duration levels at WR. During the 6 years of intensive sampling from 1997–2002, annual C-Q relations were significant for all sites and constituents.

3.2.1. Comparison of Flow-Specific Trends Analysis to Standard Methods

The SRA at 50% flow duration (SRA-50%), which reflects the median tendency and thus should agree with trends predicted by SKT and MRRA, was similar to one or the other or both standard methods for most of the solutes tested for trend (Table IV). SKT, MRRA, and the median-flow SRA results indicate similar declining trends in SO_4^{2-} concentrations at YWC for both periods tested, and at NR for the 1991–2002 period. Data was insufficient for the SRA trend test at WR, but SKT, MRRA, and the average of the high and low flow MRRA tests were similar in the long-term record. All methods at all rivers showed slightly declining or non-significant trends in NO_3^- , and increasing or non-significant trends in ALK. Long-term trends in $\text{Ca}^{2+} + \text{Mg}^{2+}$ concentrations were similar in the MRRA and SRA-50 test at WR and NR, and for the 1984–2002 period at WR, but SKT trends were higher and all tests were not significant at YWC. The SKT and SRA-50 tests yielded similar trends for the 1984–2002 period at NR, while the MRRA trend was lower.

Trends in $\text{Ca}^{2+} + \text{Mg}^{2+}$ were not significant at YWC for both the full record and the 1984–2002 period, but declining trends were significant at NR and WR.

Small positive trends in ALK concentration were indicated by all methods at NR, and at high flow at WR for the period of record.

Trends at high flow differed from trends at low and median flows for at least 2 constituents at all rivers. SO_4^{2-} trends were steeper (more negative) at high flow than at low flow at YWC and WR, and lower at high flow than at low flow at NR. Significant negative trends in NO_3^- concentration were detected at high-flow only at YWC and NR. $\text{Ca}^{2+} + \text{Mg}^{2+}$ trends were non-significant at YWC for all flows, slightly negative at all flow regimes at WR, and steeper at low flow than at high flow at NR. ALK trends for the period of record were similar among the flow-duration levels at YWC (all not significant) and NR (significant and positive), but negative at low flow and positive at high flow at WR. ALK trends at YWC and NR have been higher at high flow than low flow since 1984.

3.2.2. ANCOVA Comparison of Flow-Specific Trends

Murdoch and Shanley (in press) used SRA with 19 annual segments to test for trends during a 19-year period. The sparser data set in this study allowed only 4 segments in the same 19 years (1984–1990, 1991–1996, 1997–1999, and 2000–2002). As an alternative to evaluating 4 points for trend, we tested for statistical differences in the slope and intercept of the C-Q relation for the 4 segments through time using ANCOVA (Figure 3). Note that the x -axis is $\log(Q)$, thus the position of the y -axis ($x = 0$) is dependent on the measurement units; the resulting value of 1 cms is near the mid-range of $\log(Q)$ values.

Each line in Figure 3 represents the C-Q relation for each solute for one of the 4 time segments at each site. Five patterns are evident among the regression lines in each sub-plot: (1) Parallel/monotonic – no change in slope, but a uni-directional change in intercept, indicating that low- and high-flow trends are parallel and monotonic; (2) Parallel with reversal – no change in slope, intercept changes up and down, indicating low- and high-flow trends are parallel but trend changes direction (3) Monotonic change in slope – slope changes uni-directionally through time, indicating steepness of trend varies with flow, with no change over time at the convergence point; (4) Reversing change in slope – same as pattern 3, but slope changes non-monotonically with time; and (5) No significant change in either slope or intercept.

As an example of pattern 1, $\text{Ca}^{2+} + \text{Mg}^{2+}$ at NR maintained a constant slope, but the intercept decreased through time (except there was no significant change between the 2 middle periods), indicating that $\text{Ca}^{2+} + \text{Mg}^{2+}$ decreased uniformly at all flow levels through the period. Similarly, ALK at WR showed a monotonic upward trend at all flow levels. SO_4^{2-} at WR followed pattern 2; the earliest period had no significant C-Q relation, but, for the remaining 3 periods were significant and the intercept decreased about $10 \mu\text{eq L}^{-1}$ from its starting point, then increased back to its initial value, with no change in slope. The overall trend in SO_4^{2-} concentration at WR for the 1991–2002 period was thus not significant. SO_4^{2-} at NR showed a very similar pattern, with the intercept dropping through time before increasing at the last

segment. This relation also shows elements of pattern 3; a slight decrease in slope over time suggests that the trend is steeper at low flows compared to high flows, consistent with the numerical trend values at different flow durations (Table IV).

Though the change is not significant, ALK at NR follows pattern 3 in that slope increases with time. The lines converge at low flow, indicating that the increase in ALK is greatest at the highest flows. NO_3^- at NR is a clear example of pattern 4. From the convergence point at low flow, the slope decreases through time until

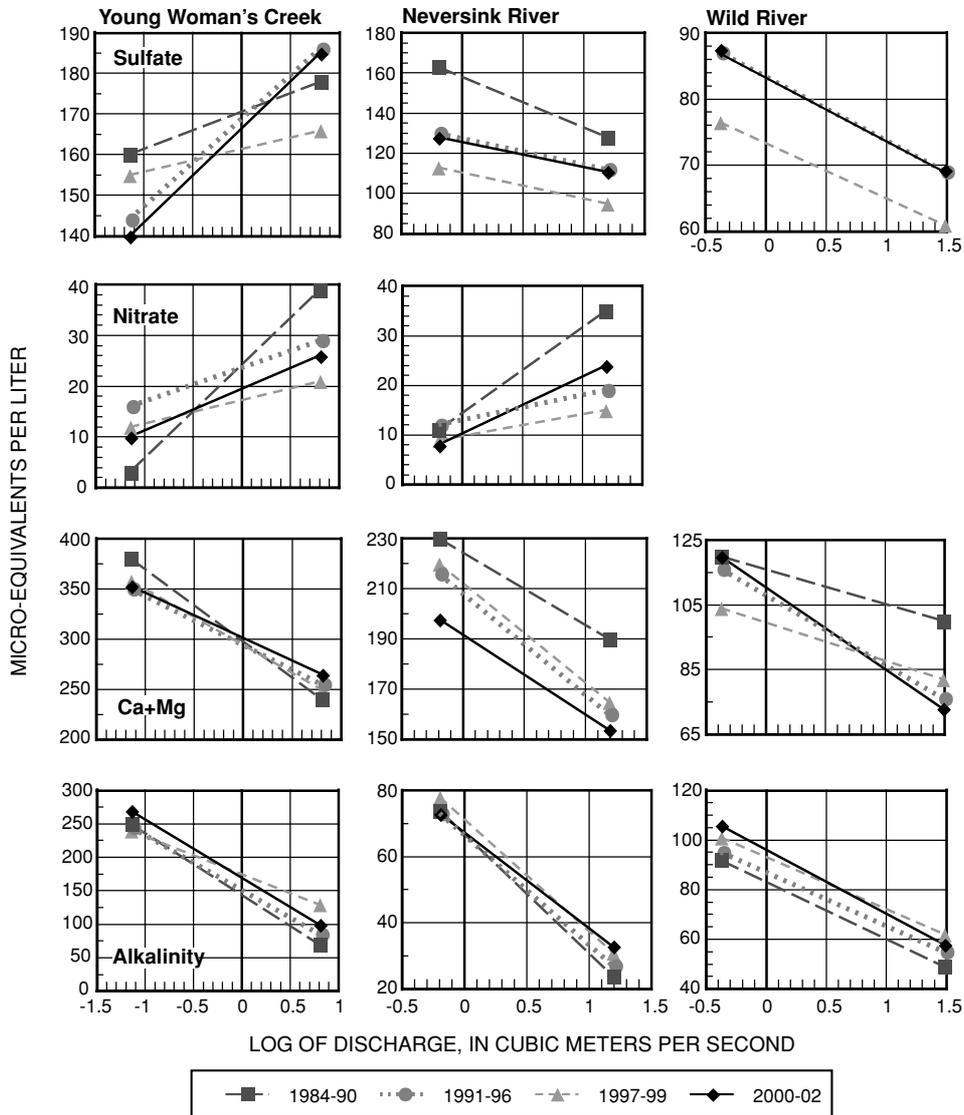


Figure 3. Average concentration-discharge relations for SO_4^{2-} , NO_3^- , $\text{Ca}^{2+} + \text{Mg}^{2+}$, and alkalinity for the periods 1984–1990, 1991–1996, 1997–1999, and 2000–2002 in the 3 study rivers.

an increase during the final period. The changes in NO_3^- concentrations clearly occurred at high flow in the NR. SO_4^{2-} and NO_3^- at YWC show a convergence point near the mid-range of flow, with shifting trends at high and low flows that are sometimes in phase and sometimes out of phase. ALK at YWC changes the least of all solutes at all sites, demonstrating pattern 5.

3.2.3. Regional Trends in Deposition

The acidity of wet deposition decreased from southwest to northeast across the study region (Table II), as did the 6-year (1997–2002) average concentrations of SO_4^{2-} , NO_3^- , and $\text{Ca}^{2+} + \text{Mg}^{2+}$. The 6-year average precipitation amount at NR was 300 mm greater than at the other two river basins because of the orographic effect of the Catskill Mountains. Mean annual loads of SO_4^{2-} for the period 1984–2002 decreased from southwest to northeast, from a maximum of $32.5 \text{ kg ha}^{-1} \text{ yr}^{-1}$ at the Kane Experimental Forest in north-central Pennsylvania to a minimum of $14.9 \text{ kg ha}^{-1} \text{ yr}^{-1}$ in Bridgeton, Maine (Figure 1 and Table II).

No significant trends in precipitation amount occurred at any of the 3 NADP stations during the 1984–2002 period (Table V). Low annual precipitation occurred during 1995 at all sites, the same year that the greatest reductions in SO_4^{2-} emissions occurred. SO_4^{2-} concentrations in precipitation also decreased at all stations used in this study in 1995 (Figure 4). The significant downward trends in SO_4^{2-} and $\text{Ca}^{2+} + \text{Mg}^{2+}$ concentrations from 1984 to 2002, indicated by SKT analysis, are consistent with those identified by Clow and Mast (1999) for 1984–1996, but the rates of decrease at all deposition stations have slowed (Table V). For example, the SEN slope estimator from the SKT trend analysis indicates that SO_4^{2-} concentration at the PA29 decreased at a rate of $1.12 \mu\text{eq/L/yr}$ during 1984–1996, but only by $0.94 \mu\text{eq/L/yr}$ during 1984–2002, suggesting either a decrease in the rate of decline or a reversal of trend during the last 6 years of the study. Part of this change may be a result of below-average precipitation in 2001–2002 at NR, but both precipitation and SO_4^{2-} concentrations in 2000 were above average at NR, and deposition volume at YWC was normal in 2000, below normal in 2001, and above normal in 2002 while sulfate concentrations were above the lowest observed concentration (1999) for all three years (Figure 4). A significant trend in NO_3^- concentration of $-0.34 \mu\text{eq/L/yr}$ occurred at PA29 during 1984–2002; no other sites showed a significant trend for either NO_3^- NH_4^+ in deposition.

3.3. COMPARISON OF TEMPORAL PATTERNS IN RIVER WATER QUALITY AT HIGH, MEDIUM, AND LOW FLOWS

Temporal patterns in SRA-generated concentrations also reveal differences in high flow and low-flow trends (Figure 5). For example, the decline in SO_4^{2-} deposition that occurred region-wide resulted in an overall decline in high and medium-flow SO_4^{2-} concentrations in YWC, but low flow concentrations rose slightly after 1995. SO_4^{2-} concentrations at NR appear to have decreased more at low flow than high

TABLE IV

Estimated annual rates of change in river-water concentrations of four constituents at the three monitoring sites in Pennsylvania, New York, and Maine, by three trend-assessment methods [Values are in microequivalents per liter per year. NS, not significant; ND, no data available; NM, no significant model; Values are for period of record. Values in parentheses are trends for water years 1984–2002, except for Neversink River SO_4^{2-} trends which are for 1991–2002.]

Method ^a	SO_4^{2-}	NO_3^-	$\text{Ca}^{2+} + \text{Mg}^{2+}$	ALK
Young Woman's Creek, Pa.				
SKT	-0.26 (-0.97)	-0.10 (-0.4)	NS (-.08)	NS (1.27)
MARRA	NS (-0.91)	NS (NS)	NS (-1.01)	NS (NS)
MARRA-<20%	NS (NS)	NS (NS)	NS (NS)	NS (NS)
MARRA->80%	NS (NS)	NS (NS)	NS (NS)	NS (NS)
SRA-95%	NS (NS)	NS (NS)	NS (NS)	NS (NS)
SRA-50%	-0.19 (-1.08)	NS (NS)	NS (NS)	NS (2.49)
SRA-5%	-0.47 (-1.77)	NS (-0.52)	NS (NS)	NS (4.22)
Neversink River, N.Y.				
SKT	-0.91 (-2.40)	-0.31 (-1.17)	-2.23 (-2.42)	0.80 (0.71)
MARRA	-0.96 (-2.03)	0.11 (-0.62)	-1.10 (-1.55)	0.97 (0.64)
MARRA-<20%	ND (-1.74)	0.14 (-0.70)	-1.45 (-1.54)	0.77 (0.37)
MARRA->80%	ND (-2.06)	NS (-0.36)	-0.84 (-1.34)	1.21 (NS)
SRA-95%	ND (-3.10)	NS (NS)	-1.90 (-3.29)	1.01 (NS)
SRA-50%	ND (-2.53)	NS (NS)	-1.22 (-2.40)	0.96 (0.49)
SRA-5%	ND (-2.03)	NS (-1.26)	NS (-1.41)	0.92 (0.94)
Wild River, Maine				
SKT	-1.08 (-1.24)	-0.10 (NS)	-1.30 (-1.50)	-0.10 (NS)
MARRA	-1.14 (-1.16)	NM (NM)	-1.01 (-1.08)	NS (NS)
MARRA-<20%	-1.22 (NS)	NM (NM)	NS (NS)	NM (NM)
MARRA->80%	-0.75 (NS)	NM (NS)	-0.67 (NS)	-0.79 (NS)
SRA-95%	NM (NS)	NS (NS)	-1.01 (-1.10)	-0.88 (NS)
SRA-50%	NM (NS)	NS (NS)	-0.97 (-1.10)	NS (NS)
SRA-5%	NM (NS)	NS (NS)	-0.95 (-1.11)	1.24 (NS)

^aSKT, seasonal Kendall's Tau; MARRA, multiple regression residual analysis: <20%, less than 20% flow duration; >80%, greater than 80% flow duration; SRA, segmented regression analysis: 95% duration = low flow; 50% duration = medium flow, 5% duration = high flow.

flow between the mid-1980s and late 1990s, and stabilized or reversed trend at high flow since 1998. NO_3^- concentrations in NR rose at high and medium flows during the 1970s, and at YWC during the 1980s, but low-flow concentrations remained near previous levels. In contrast, low-flow NO_3^- concentrations rose faster than high-flow concentrations in the late 1980s at NR, and declined at a slower rate thereafter resulting in a convergence of NO_3^- concentrations at high and low flows at the end of the record. $\text{Ca}^{2+} + \text{Mg}^{2+}$ trends at YWC for the period of record were

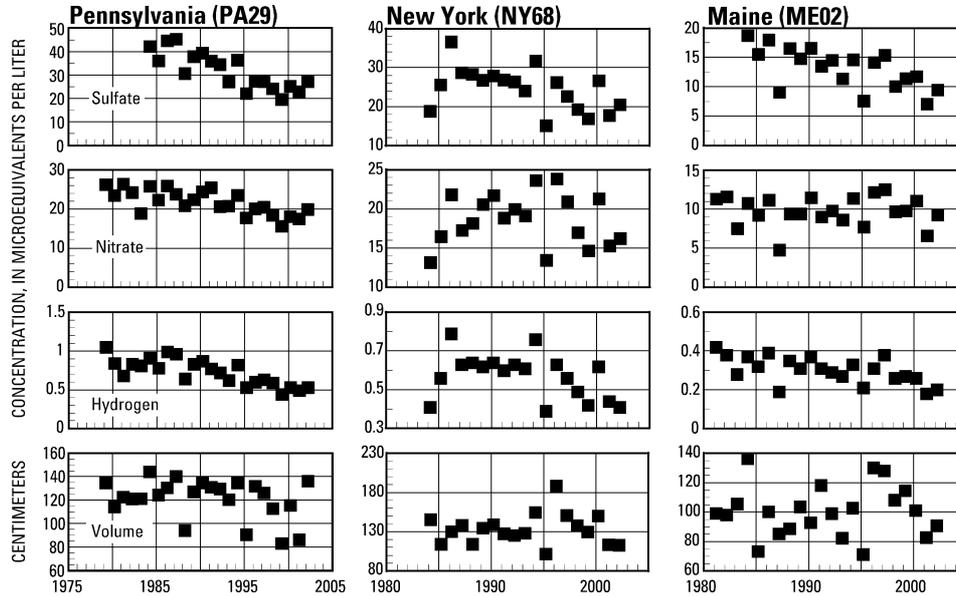


Figure 4. Annual average concentrations of SO_4^{2-} , NO_3^- , and Hydrogen ion in deposition, and annual precipitation volume at the nearest National Trends Network station to each of the study watersheds.

small or not significant at all flows; concentrations decreased over time at all flows at NR and WR, and the range of concentrations among the flow duration levels decreased. The greatest high-flow $\text{Ca}^{2+} + \text{Mg}^{2+}$ concentrations at NR occurred during the early 1970s and late 1980s. ALK concentrations have been relatively steady at all flows since the early 1970s, but appear to have increased slightly at all flows since 1995 at YWC and NR.

4. Discussion

4.1. USE OF FLOW-SPECIFIC TREND ANALYSIS WITH SPARSE DATA SETS

Despite the limited data available from the HBN sites prior to 1997, C-Q relations were statistically significant for a sufficient number of temporal segments to assess flow-specific trends. Compilation of multiple-year segments was required to develop significant relationships, so the length of record required to assess trends was longer than if yearly C-Q relations could be established. If we apply the general requirement of a minimum of 8 years of record for assessing trends as recommended by Helsel and Hirsch (1992) for SKT trend analysis, most of the SRA trends created in this study had more than 8 segments. Exceptions occurred at WR, where NO_3^- concentrations were seldom above detection, and a significant C-Q relationship for SO_4^{2-} could not be established prior to the mid 1990s. C-Q relations for SO_4^{2-} could be established for the entire period of record at WR, however, using the flow-class

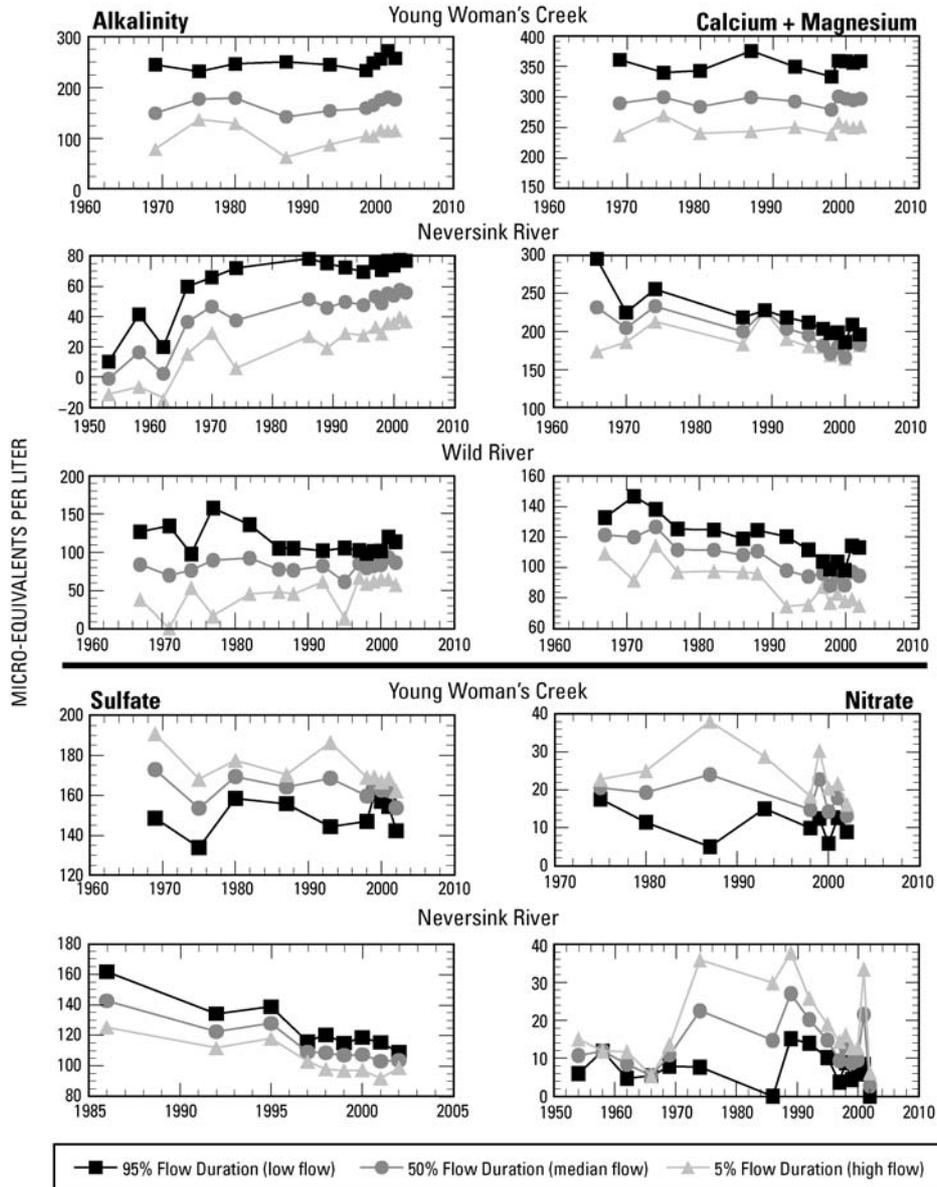


Figure 5. Concentrations of SO_4^{2-} , NO_3^- , $\text{Ca}^{2+} + \text{Mg}^{2+}$, and alkalinity at high, medium, and low flow in each data segment as determined by SRA for the 3 study streams.

MARRA method, which provided an alternative flow-specific trend analysis where segmented regressions were not statistically valid.

Trends determined for median-flow conditions using the SRA methods were also generally consistent with trends determined by flow-adjusted SKT (Table IV). Exceptions were ALK at YWC, where SRA-50% predicted double the SKT trend,

and SO_4^{2-} at WR, where significant C-Q relations for SO_4^{2-} could not be established prior to 1991. The concept of using sequential, segmented C-Q regression models as a tool for assessing trends at specific river discharges therefore has application for long-term river monitoring data if (a) sufficient data are collected within each temporal segment to define a statistically-significant concentration-discharge relationship, and (b) the number of segments with significant C-Q relations are sufficient to determine a statistically-valid trend at each flow-duration level.

4.2. HIGH-FLOW TRENDS AS INDICATORS OF RECENT CHANGES IN DEPOSITION

SO_4^{2-} deposition rates in the study region decreased from 1984 to 2002 at all three stations based on SKT analysis, but the rate of decline slowed during 1996–2000 in Pennsylvania and southeastern New York (Table V and Figure 4). Trends in river SO_4^{2-} concentrations determined by SKT also indicated declining concentrations for the 1984–2002 period at all 3 rivers, although the SKT trend at NR was not significant at $p < 0.05$ and the rate of change at YWC and NR declined from 1996 to 2002 (Tables V and VI; Figure 4). The ANCOVA analysis indicated an increase in stream SO_4^{2-} concentrations after 1999 at all flows in NR and WR, and at high and medium flows at YWC, compared to the 1997–1999 period (Figure 3). The SO_4^{2-} concentrations determined using SRA at YWC and NR and FC-MRRA at WR therefore varied over time in a manner that was consistent with observed deposition trends.

The negative SRA trends for SO_4^{2-} concentration were larger at low flows than at high flows at NR during 1991–2002, where lower median-flow concentrations for the 1997–1999 segment than for the 2000–2002 segment were also indicated at all flows (Table IV, Figures 3, 5). These results are consistent with a change in deposition rates at the end of the record (Figure 4, Table V), which would be expected to affect stormflow runoff before affecting groundwater concentrations. In this case, an increase or stabilization of SO_4^{2-} deposition rates during the last 5 years of record appears to have slowed the long-term trend of decreasing high-flow concentrations in streamwater, while trends in low flow concentrations remained unchanged. Likewise, increased high-flow SO_4^{2-} concentrations in YWC between the 1984–1990 and 1991–1996 segments were followed by increased low-flow concentrations in 1997–1999, implying that surface runoff in 1991–1996 infiltrated and increased groundwater concentrations in succeeding years (Figure 5). Climate or deposition-related change in river-water quality is expected first at high flows, which are generated by surface and shallow-soil runoff, whereas a lag is expected before the change is transmitted to groundwater reservoirs that control base flow.

At YWC, however, declining SO_4^{2-} trends in high flow concentrations were steeper than trends at lower flows. YWC, which is south of the southern-most extent of glaciation, has older soils than at NR and WR, and thus greater SO_4^{2-} adsorption capacity, larger SO_4^{2-} pools, and longer SO_4^{2-} residence times than soils

TABLE V
 Rates of change and significance of trends (p) in precipitation volume and concentration of selected constituents at the three National Trends Network stations, based on Seasonal Kendall's Tau (SKT) test

Station	Dates	Volume	p	Constituents										
				SO_4^{2-}	NO_3^-	p	NH_4^+	p	$\text{Ca}^{2+} + \text{Mg}^{2+}$	p	H^+	p		
PA29	1984-1996	0	1	-1.12	0.001	-0.35	0.13	0.13	-0.12	0.29	-0.23	0.004	-1.07	0.008
	1984-2002	-0.03	0.46	-0.94	0	-0.34	0.006	0.006	-0.07	0.47	-0.16	0	-1.02	0
NY68	1984-1996	0.07	0.46	-1.05	0.002	-0.05	0.66	0.66	0	1	-0.20	0.001	-0.75	0.19
	1984-2002	0.02	0.74	-0.87	0	-0.13	0.37	0.04	0.68	-0.10	0.001	-0.73	0.005	
ME02	1984-1996	0.01	0.97	-0.63	0.006	0.01	0.97	0.12	0.17	-0.13	0.03	-0.25	0.44	
	1984-2002	0.06	0.26	-0.61	0	0.08	0.42	0.12	0.026	-0.06	0.06	-0.26	0.09	

Rates of change are in microequivalents per liter per year. Locations are shown in Figure 1.

TABLE VI
Rates of change and significance of trends in stream discharge and concentration of selected constituents at the three monitoring sites in Pennsylvania, New York, and Maine, based on Seasonal Kendall's Tau (SKT) test

River	Dates	Discharge	Constituents											
			SO ₄ ²⁻	NO ₃ ⁻	ALK	Ca ²⁺ + Mg ²⁺	H ⁺	p	p	p	p	p	p	
YWC	1967-2002	-0.38	0.016	0.14	0.05	0.03	0.16	0	0.61	-0.003	<0.001			
	1984-1996	1.26	0.12	0.14	0.14	1.07	0.12	-0.90	0.25	0	0.94			
	1984-2002	0.03	0.89	0.007	0.03	1.27	0.008	-0.80	0.09	0.005	0.004			
NR	1971-2002	0.08	0.86	0.001	0.006	0.80	<0.001	-2.23	<0.001	0	0.60			
	1984-1996	-3.00	0.19	<0.001	<0.001	0.73	0.004	-2.37	<0.001	-0.02	<0.001			
WR	1984-2002	1.43	0.34	0.24	<0.001	0.71	<0.001	-2.42	<0.001	0	0.48			
	1964-2002	0.72	0.058	<0.001	<0.001	-0.10	0.05	-1.3	<0.001	0	0.90			
	1984-1996	-0.90	0.60	0.10	0.90	-0.93	0.17	-1.5	0.001	0.009	0.18			
1984-2002	-0.63	0.60	<0.001	0.40	0.12	0.80	-1.5	<0.001	0.013	0.002				

YWC, Young Woman's Creek, Pa.; NR, Neversink River, N.Y.; WR, Wild River, Maine. Rates of change are in microequivalents per liter per year. Locations are shown in Figure 1.

in the glaciated watersheds to the north (Mast and Turk, 1999). Groundwater SO_4^{2-} concentrations at YWC can therefore be sustained by leaching of stored SO_4^{2-} for an extended period following declines in deposition. Groundwater SO_4^{2-} concentrations are thus more responsive to increases or decreases in SO_4^{2-} deposition in the NR basin than in the YWC basin. The MRRA-FC also indicated that SO_4^{2-} concentration was decreasing faster at high flows than at low flows at Wild River (Table IV). However, SO_4^{2-} deposition at WR continued to decline at a steady rate during the last 5 years of record, so the steeper trends in river SO_4^{2-} concentrations at high flows fits the conceptual models of deposition changes affecting high-flow river concentrations before those at low flow.

Both the temporal patterns in the SRA results and the ANCOVA analysis of segmented C-Q relations for NO_3^- indicate contrasting trend patterns at high and low flow at both YWC and NR (Figures 3, 5). At NR, NO_3^- concentration changes have been dynamic since the mid-1980s at high flows, while changes were more muted at low-flow. At YWC, high concentrations at high flow from 1984–1990 were followed by elevated concentrations at low flow from 1991–1996. The high export of the 1970s at high and medium flows at NR did not appear to affect base-flow concentrations, but increases in high and medium flow concentrations in the late 1980s resulted in an immediate response in baseflow concentrations. The reason for this difference is not clear from the available data; the high NO_3^- flux of the 1970s followed an extended period of drought and was concurrent with the peak period for nitrogen deposition in the northeastern United States, while the late 1980s high NO_3^- flux was associated with warmer-than-average air temperatures and increased microbial processing of N in soils (Murdoch *et al.*, 1998). Perhaps NO_3^- in deposition that has accumulated during drought conditions is more likely to be washed directly into the surface waters during rainstorms and snowmelt, while NO_3^- generated from soil processes is more likely to infiltrate into the groundwater system. Whatever the explanation, tracking of trends at high and low flow conditions could allow improved understanding of how nitrogen moves through forested watersheds.

YWC showed little or no change in $\text{Ca}^{2+} + \text{Mg}^{2+}$ concentrations through time, and had higher concentrations than at NR and WR, where the concentrations decreased over the period of record (Figure 5). Comparison of the 6-year SRA segments for NR using ANCOVA indicated that concentrations at high, medium, and low flows decreased at relatively uniform rates from 1984 through 2002. $\text{Ca}^{2+} + \text{Mg}^{2+}$ concentrations in WR showed a decrease at high flows in the early 1990s that was not observed in low flows till the mid 1990s.

The constituent with the greatest number of significant 3-year segments at all the study rivers was ALK, which was also the constituent with the least number of irregularities and data gaps in the record (Figure 5). ALK concentration trends imply an increase in concentrations since the mid 1980s at high and medium flows duration levels in NR, and at high and medium flows at YWC and WR. Again, declining acidity in deposition would be expected to affect high and medium flow

ALK concentrations before affecting concentrations at baseflow. The SKT analysis identified significant upward trends at YWC and NR for 1984–2002 and a nonsignificant upward trend at WR. ALK of soil water and groundwater in the relatively well buffered environment at YWC would be expected to be stable in the deep soil horizons but subject to acidity from deposition in the upper soil. The steeper long-term increasing trend in river ALK at YWC for high flows relative to low flows is consistent with a decrease in SO_4^{2-} and NO_3^- concentrations in atmospheric deposition since the 1980s.

4.3. OPTIMUM SAMPLING STRATEGY FOR TREND DETECTION

The annual number of samples needed to assess water-quality trends at specific flows depends on the strength of the C-Q relation and the resolution of the trends required by the user. Trend analysis that is segmented by flow class, as in the MRRA method, requires a sufficient number of samples within each class, distributed over the period of record, to generate statistically significant models. Segmentation of the data into time periods, as in the SRA method, requires sufficient sampling to define the concentration-to-discharge relation within each time segment, but because the method uses all samples collected in all flow classes, it requires fewer samples within an extreme-flow class than the MRRA to estimate a concentration-to-discharge relation for that class. The accuracy of the SRA will be compromised, however, if seasonality in the C-Q relation is not adequately incorporated, or if the overall C-Q relation is poor. Bias of annual segments can probably be avoided by sampling a range of flow conditions within each season of the year. Each trend-monitoring site will initially need to be sampled frequently over a range of flow conditions to determine the specific sampling requirements of that stream. The SRA for $\text{Ca}^{2+} + \text{Mg}^{2+}$ based on 3-year segments at WR yielded less significant regression equations and more variability in the trends than did the 6-year segments. The 6-year segments included more analyses per regression and covered a broader range of seasonal conditions and flows than the 3-year segments and, thus, averaged the short-term variability inherent in the river water-quality.

5. Conclusions

The results in this study illustrate that mesoscale (25–250 km²) watersheds are directly influenced by the effects of acidic deposition, and are meaningful landscapes for tracking changes related to the mitigation of air pollution through the CAAA. Increases in stream ALK are clearly associated with decreases in SO_4^{2-} and NO_3^- deposition, but reversal of these improvements can occur rapidly, even in mesoscale watersheds, if acid deposition increases. By compiling data from multiple years that represent the range of flow conditions that occurred in these rivers, segmented concentration-discharge relations can be used to track trends in stream

water quality at specific flow-duration levels. This analysis showed that there can be significant differences in water quality trends at high and low flow conditions in large rivers, and that changes in river water quality resulting from reductions in acidic deposition can be detected as trends in high-flow concentrations using flow-specific trend analysis before they are detected by other methods of trend detection.

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