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Detection of water quality trends at high, median, and low flow in a Catskill Mountain stream, New York, through a new statistical method

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[1] The effects of changes in acid deposition rates resulting from the Clean Air Act Amendments of 1990 should first appear in stream waters during rainstorms and snowmelt, when the surface of the watershed is most hydrologically connected to the stream. Early detection of improved stream water quality is possible if trends at high flow could be separately determined. Trends in concentrations of sulfate (SO_4^{2-}), nitrate (NO_3^-), calcium plus magnesium ($Ca^{2+}+Mg^{2+}$), and acid-neutralizing capacity (ANC) in Biscuit Brook, Catskill Mountains, New York, were assessed through segmented regression analysis (SRA). The method uses annual concentration-to-discharge relations to predict concentrations for specific discharges, then compares those annual values to determine trends at specific discharge levels. Median-flow trends using SRA were comparable to those predicted by the seasonal Kendall tau test and a multiple regression residual analysis. All of these methods show that stream water SO_4^{2-} concentrations have decreased significantly since 1983; $Ca^{2+}+Mg^{2+}$ concentrations have decreased at a steady but slower rate than SO_4^{2-}; and ANC shows no trend. The new SRA method, however, reveals trends that differ at specified flow levels. ANC has increased, and NO_3^- concentrations have decreased at high flows, but neither has changed as significantly at low flows. The general downward trend in SO_4^{2-} flattened at median flow and reversed at high flow between 1997 and 2002. The reversal of the high-flow SO_4^{2-} trend is consistent with increases in SO_4^{2-} concentrations in both precipitation and soil solutions at Biscuit Brook. Separate calculation of high-flow trends provides resource managers with an early detection system for assessing changes in water quality resulting from changes in acidic deposition.

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1. Introduction

[2] The Clean Air Act of 1970 and the subsequent Clean Air Act Amendments (CAAA) of 1990 marked the beginning of a long-term global experiment in the reversal of environmental damage caused by air pollution. The amendments called for (1) a 50% decrease in SO_2 emissions by utilities to below 1980 levels by 2010 and (2) an annual emission rate limitation for NO_x emissions of 0.39 lbs of NOx/M BTU (million British thermal units) [*Driscoll et al.*, 2001; *U.S. Government Accountability Office*, 2000]. These decreases in sulfur and nitrogen emissions from industrial sources were ordered to begin in 1995 and to be completed by 2010. A new pollution reduction strategy, the "Clear Skies" initiative, is now under review, and interim clean air rules have been implemented by USEPA (J. Stoddard, Environmental Protection Agency, oral communication, 2005).

[3] Determining whether this nationwide effort in pollution reduction is having the desired effect requires systematic monitoring of environmental conditions in the preimplementation, implementation, and postimplementation phases, and statistical analyses that can detect often subtle environmental responses to those pollution reductions. Established methods of trend detection, however, generally require 8 years to be considered statistically valid [*Helsel and Hirsch*, 1992]. Resource managers typically need to know if their management decisions have been effective before 8 years have elapsed. Detecting short-term trends in the quality of surface waters is therefore an essential ingredient to timely determination of the success or failure of the air pollution management strategies.

[4] Deposition of NO_3^- stabilized and SO_4^{2-} declined in the northeastern U.S. during the 1990s [*Stoddard et al.*, 2003], but the effects of these improvements on surface water quality have been slow to appear, and the processes that control stream response to changes in air quality are complex and difficult to quantify [*Stoddard et al.*, 1999]. For example, stream water samples collected in the northeastern U.S. during rapidly changing flow conditions indicate that NO_3^- concentrations increase rapidly during stormflows and return to normal within a few days after

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the storm or snowmelt period ends [*Murdoch and Stoddard*, 1992]. Landscape physiography, soil chemistry and transmissivity, hydrologic flow paths, climate, and precipitation amount and distribution all affect how changes in acidic deposition affect stream water quality [*Bishop et al.*, 1990; *Clow and Mast*, 1999; *Murdoch et al.*, 1998]. The theoretical steps by which watersheds and streams become acidified by deposition, as described by *Aber et al.* [1989] and *Stoddard* [1994] suggest that stream acidification will initially be observed during high-flow events as acids are flushed via shallow flow paths from the upper soil into streams. *Stoddard* [1994] hypothesized that chronic acidification results when these acidification episodes expand in duration and acidic soil waters percolate into groundwater reservoirs. Similarly, a decrease in the acidity of deposition would first result in a decrease in the acidity of shallow soil water and stormflow, and would eventually result in a decrease in the acidity of groundwater and base flow. A reliable assessment of the early effects of the CAAA and Clear Skies Initiative on stream water quality would thus require sufficient data to assess whether surface water acidity at high-flow conditions was changing through time.

[5] This study presents a new method for determining flow-specific trends in water quality. The segmented regression analysis (SRA) is a regression model approach to trend detection that allows trend analysis at specific streamflow levels, while minimizing the sampling required for high-flow trend detection. Trends at high-, median-, and low-flow conditions determined by the SRA are compared to trends derived from the same data set using the flow-adjusted seasonal Kendall's tau (SKT) test, and from residuals of a multiple-regression model that considers the effects of other potential controlling factors on water quality besides discharge. Finally, the results are used to assess the effects of the CAAA on deposition and stream water quality in a headwater watershed of the Catskill Mountains in southeastern New York. The method development and analysis is based on an intensive data set collected at Biscuit Brook during both stormflow and base flow over 18 years from October 1984 through September 2002. Objectives of the study were (1) to test whether trends, or changes in trends, are specific to a given flow range (high, median, low) and (2) to document the initial effects of the CAAA on deposition and stream water quality in the study watershed.

1.1. Established Methods of Trend Detection

[6] Numerous papers on trends in surface water quality have been published in recent years [e.g., *Esterby*, 1996; *Clow and Mast*, 1999; *Driscoll et al.*, 2001]. The most common method for assessment of trends in stream water quality is the nonparametric seasonal Kendall's tau (SKT) test, which detects monotonic (unidirectional) trends over time in data that can be nonnormally distributed but contain seasonal patterns [*Hirsch et al.*, 1982; *Hirsch and Slack*, 1984; *Mattson et al.*, 1997; *Stoddard et al.*, 1998, 1999; *Clow and Mast*, 1999; *Evans et al.*, 2001; *Driscoll et al.*, 2003]. The SKT test does not compute a slope—most studies use the Sen slope estimator [*Sen*, 1968], which summarizes the differences in concentration between all adjacent "seasons" (October 1998 versus October 1999; October 1999 versus October 2000, etc.) to create an overall slope for the period of record [*Clow and Mast*, 1999]. Other studies have determined trends through graphical locally weighted scatterplot smoothing (LOWESS) techniques coupled with regression analysis of the deviations from the LOWESS curve over time [*Robson and Neal*, 1996; *Qian et al.*, 2000; *Watt et al.*, 2000; *Lawrence et al.*, 2004]. In other studies where normality of the data relative to time could be assumed, trends were computed from the slope of the regression between concentration and time [*Watt et al.*, 2000; *Stoddard et al.*, 2003]. Common to these methods is the need for fixed-interval sampling (typically weekly to quarterly), with the objective of determining long-term trends in water quality at base flow or average (random) flow conditions [*Clow and Mast*, 1999; *Driscoll and Van Dreason*, 1993; *Smith and Alexander*, 1983].

[7] None of the methods described above were designed to assess trends in water quality during specific flow conditions. Flow-adjusted SKT trends [*Hirsch and Slack*, 1984; *Helsel and Hirsch*, 1992] remove the effect of flow from the trend determination, but do not provide for differentiation of trends at specific flow levels. LOWESS techniques create a concentration timeline by comparing temporally adjacent samples, and thus are also significantly affected by sampling intensity and seasonal representation [*Aulenbach et al.*, 1996]. Sampling of every stormflow or snowmelt event is prohibitively expensive and logistically infeasible for most monitoring programs. To separately assess trends during high-flow conditions, a method for allowing representative rather than complete sampling of the stream hydrograph is needed.

1.2. Study Area

[8] The data for this analysis were collected in the Biscuit Brook watershed (9.98 km^2), a headwater basin that drains into the Neversink River and ultimately into the Delaware River and Delaware Bay (Figure 1). Biscuit Brook has been monitored for discharge and water quality by the U.S. Geological Survey (USGS) since 1983 and was a USGS Hydrologic Benchmark station from 1988 through September 1997. The headwaters area is steep; the watershed is 100% forested and has not been logged for at least 60 years [*Murdoch*, 1991]. Forest type is predominately mixed hardwoods, with spruce and fir along the ridge tops and small patches of hemlock along the stream. Watershed geology consists of flat-lying beds of sandstone, shale, and conglomerate, with two 90° vertical joint fracture sets that create a block-like structure and preferential flow paths for groundwater [*Murdoch*, 1991]. Soil lysimeters described later are located in an adjacent watershed with similar bedrock and soil characteristics. Average annual air temperature is 5°C, and snow cover typically lasts from mid-December through mid-March. Detailed descriptions of the watershed are given by *Murdoch* [1991] and *Lawrence et al.* [2001].

2. Methods

2.1. Sample Collection and Analysis

[9] Biscuit Brook has been monitored continuously for discharge and water temperature (15-min recording interval) since October 1983 by standard USGS methods [*Rantz*, 1982]. Weekly water quality samples have been collected manually, and sequential samples have been collected by an automated sampler during snowmelt and rainstorms, since 1983. Water samples were typically retrieved within

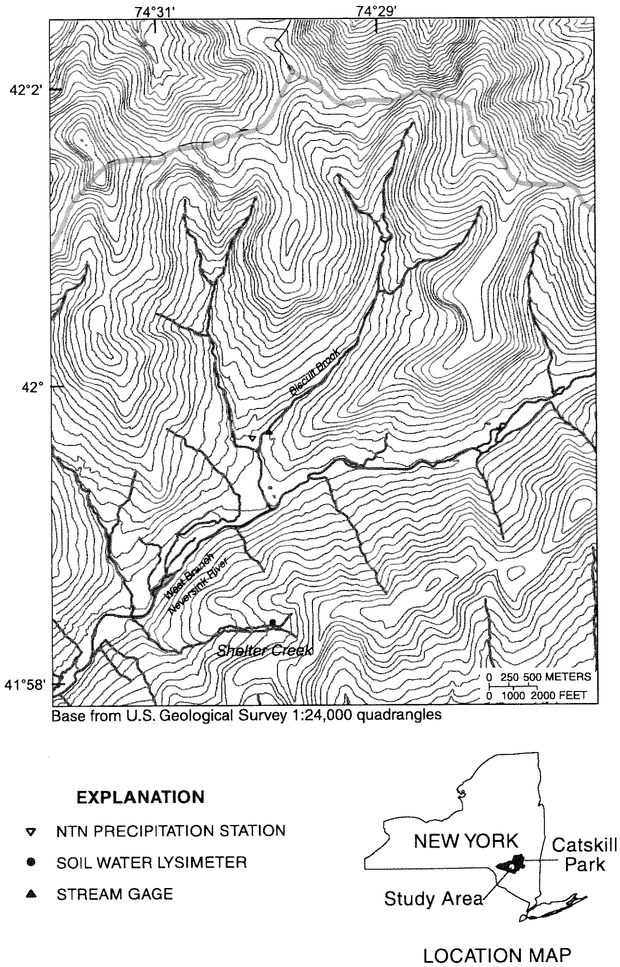

Figure 1. Map of the Biscuit Brook watershed and USGS soil lysimeter locations in southeastern New York.

48 hours of sample collection, chilled, and transported to the USGS laboratory in Troy, N.Y. for processing and distribution to analytical laboratories.

[10] Samples were analyzed since 1991 at the USGS research laboratory in New York for major solutes; solutes discussed in this paper include the sum of calcium and magnesium (Ca^{2+}+Mg^{2+}), sulfate (SO_4^{2}), nitrate (NO_3^-), and acid-neutralizing capacity (ANC). ANC was determined by Gran titration [*Gran*, 1952]. Methods used before 1997 are documented by *Lawrence et al.* [1995], and methods used since 1997 are documented by *Lawrence et al.* [2001]. Samples collected prior to 1991 were analyzed for anions and ANC at the same USGS laboratory mentioned above, then located in Albany, N.Y. Cation analyses were conducted prior to 1991 at the USGS Central Analytical Laboratory in Arvada, Colorado by methods consistent with those used since 1991 in the USGS laboratory in N.Y. [*Fishman and Friedman*, 1985]. Laboratory comparison studies have shown no significant bias in the data used for this study (G. Lawrence, written communication, 2002).

[11] Weekly precipitation volume and wet-only chemistry data were available from the National Trends Network (NTN) station NY68 in the lower part of the Biscuit Brook watershed. The NTN station was established in 1983 at the same time as the stream-monitoring station (Figure 1). Field monitoring methods were consistent with National Acid Deposition Program (NADP) protocols. Precipitation amount was measured at each site with a weighing-bucket rain gage, and samples were analyzed at the NADP Central Analytical Laboratory (CAL) in Champaign, Ill. Solutes reported in this paper include Ca^{2+}+Mg^{2+}, SO_4^{2-}, NO_3^-, and ammonium (NH_4^+). Analytical methods and QA/QC are reported on the NADP Web site (http://nadp.sws.uiuc.edu, accessed April 2003).

[12] Supporting evidence for assessing stream water trends was also developed by monitoring soil solution chemistry from 1992–2002 in a similar watershed 2 km east of Biscuit Brook [*Murdoch et al.*, 2005]. Zero-tension lysimeters were installed below the B soil horizons (30 cm depth), and solution samples were collected biweekly to monthly. Each lysimeter consisted of three 15-cm diameter convex pans (603 cm^2 total collection area) spaced at least 30 cm apart, at similar depth in the soil, and connected to a common collection vessel.

2.2. Quality Assurance and Quality Control

[13] Quality assurance and quality control (QA/QC) data for the USGS laboratory are published by *Lincoln et al.* [2001, 2004]. Quality control samples, interlaboratory audit samples, and blanks met the data quality objectives (DQOs) in >95% of the tests conducted [*Lincoln et al.*, 2004]. One set of triplicate samples was collected in the field for every 50 or fewer samples. The DQO for triplicate samples was a coefficient of variation of less than 10%. Samples were also collected quarterly by the depth-integrated, equal-area method (standard USGS protocol described by *Edwards and Glysson* [1988]) at the same time as the automatically collected samples to test the comparability among automated, depth-integrated, and manual grab samples. No systematic bias among sampling methods was found (G. Lawrence, USGS, written communication, 2003).

2.3. Methods of Trend Analysis

[14] Concentration-discharge (C-Q) relationships have long been used to calculate sediment and chemical loads in streams and rivers [*Johnson et al.*, 1969; *Dann et al.*, 1986; *Murdoch*, 1991; *Murdoch et al.*, 1998; *Edwards et al.*, 2003]. Inherent in this method is the assumption that the relationship between flow and concentration is consistent over the period of interest (decade, year, season, etc), so that selected samples that span the range of flows observed during that period can be used to estimate concentrations at all flows when samples were not collected. A significant C-Q relationship allows for a logistically and fiscally feasible sampling program to be developed. It stands to reason that if a long-term data set can be split into temporal segments, such that each segment has sufficient data to generate a significant C-Q relationship, then concentrations at high, median, or low flow could be compared among the segments for determining trends. This concept forms the basis of our Segmented Regression Analysis (SRA).

[15] SRA was performed by using 1-year segments (19 total segments) of continuous discharge and flow-distributed water quality data from Biscuit Brook to create linear regression models for each segment, from which estimated concentrations at a specific discharge in each data segment could be calculated. Specified discharges for com-

parison among the segments were selected by computing a flow duration curve for the entire period of record for discharge at Biscuit Brook, and selecting discharges at the 5% (high-flow), 50% (median-flow) and 95% (low-flow) duration levels. A flow duration level of 95% is the discharge that is equaled or exceeded 95% of the time during the computation period. Flow duration curves based on discharges at the times of sample collection were relatively consistent with flow duration curves based on the entire 15-min discharge record, indicating representative sampling over the hydrograph. The annual concentrations at specified flows were then tested for trend by linear regression.

[16] Although this study had sufficient data to compute significant ($p < 0.005$) C-Q relations for an annual segment, longer segments of time could be used for sparser data sets or for specific statistical tests. The assumption in this approach is that while multiyear patterns in high-flow chemistry may be masked by the effects of short-term climatic, seasonal, or storm-to-storm variability, shifts in the slope and intercept of a sequentially computed concentration-to-discharge relation can transcend this "noise" and thus reveal trends at specified discharges. To test the validity of this new method of trend detection, and the hypothesis that different flow regimes have different water quality trends, we determined that the following criteria should be met:

[17] 1. The concentration trends at median flows for the period of record should be similar in magnitude and direction to the trends determined by accepted methods of trend detection.

[18] 2. An Analysis of Covariance (ANCOVA) test should indicate significant differences among the temporal segments in the slope and/or intercept of concentration-discharge regression equations.

[19] 3. Temporal patterns in the flow-specific, annual average concentrations predicted by the SRA should be scientifically defensible on the basis of our knowledge of watershed biogeochemistry, hydrology, and observed patterns in precipitation chemistry.

[20] Methods used to assess each of these criteria are described below. For each flow level considered, the reported trend slope, calculated from the time series of predicted segment (in this case, annual) concentrations in the SRA, represents an aggregate measure of the long-term change in flow-conditioned concentrations. Estimates of the statistical uncertainties associated with the SRA-based trend slope were not made as part of this analysis. Uncertainty estimates could be developed as part of future improvements in the SRA methodology, such as through the use of Monte Carlo techniques that would fully account for the model coefficient error and the residual error associated with the model predictions of flow-conditioned concentration. Individual segment concentrations for 5% or 95% duration flows have lower confidence if those flows are not observed in that segment. However, an SRA-predicted trend based on all of the observed concentrations and flows in each year will describe changes that would have occurred that year had those specified flows actually been observed.

2.3.1. Criterion 1: Comparison of Period-of-Record Trends

[21] Two methods of average flow trend detection were compared with the SRA results for the period of record. A brief description of each method is provided, followed by an explanation of how the results from each method were related in this study.

2.3.1.1. Nonparametric Seasonal Kendall's Tau (SKT) Analysis

[22] The SKT statistic [*Schertz et al.*, 1991; *Helsel and Hirsch*, 1992] was determined for stream water and deposition collected within the Biscuit Brook watershed. A monthly time step, or "season," was used for both the stream water and deposition analyses; both flow-adjusted and non-flow-adjusted trends were assessed. The sample closest to midmonth was selected by the model to represent that month. The slope of the SKT trend was defined as the median of the slopes among the set of seasonal pairwise comparisons (e.g., October 1991 versus October 1992 [*Sen*, 1968]) Trends in precipitation amount and stream discharge were also determined by SKT for this study.

2.3.1.2. Multiple Regression Residual Analysis (MRRA)

[23] Multiple-regression residual analysis (MRRA) required 2 steps: (1) optimization of an empirical multiple-regression concentration model for each solute that used average antecedent discharge and seasonal terms [*Aulenbach and Hooper*, 2006; *Huntington et al.*, 1994] and (2) analysis of temporal trends in the model residuals. Note that we used the approach of *Aulenbach and Hooper* [2006] for the concentration models only (i.e., we did not calculate loads), and that time was purposely excluded from the models so that any temporal trends would appear in the model residuals. The discharge term was the Johnson flow model term [*Johnson et al.*, 1969] of the form $1/(1 + \beta Q_a)$, where Q_a is the discharge averaged over an antecedent period "a" prior to sampling, and β is a constant. For each sample, Q_a was calculated for $a = 0$, 1, 6, and 12 hours and for 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 both sine and cosine terms allowed the optimization of the amplitude and phase of each seasonal signal. The half-sine and half-cosine terms accounted for short-term variability. Residuals of the models were analyzed for trends using linear regression.

2.3.1.3. Validation of SRA

[24] The slope of the SRA-generated trends for the period of record were compared to the Sen slope estimator computed from the SKT trend analysis, and the slope of the linear regression determined by the MRRA. Similarity in the direction and magnitude of the SRA trend at the 50% flow duration level to the SKT and MRRA trends for each constituent was considered validation of the SRA method.

2.3.2. Criterion 2: Analysis of Covariance (ANCOVA)

[25] A three-way ANCOVA test was applied to a three-segment SRA of the 18-year data set from Biscuit Brook. The data were split into one 7-year and three 6-year segments by water year (WY, 1 October of the previous year to 30 September of the designated water year) (WY84-90, WY91-96, WY97-02). Concentration discharge relations for each constituent were computed separately for each segment, and differences in the slope and y intercept of the regression equations for each segment were tested for significance [*Helsel and Hirsch*, 1992]. Differences in the y intercept of the regression equations without a change in slope indicate a trend in water quality that is consistent at all

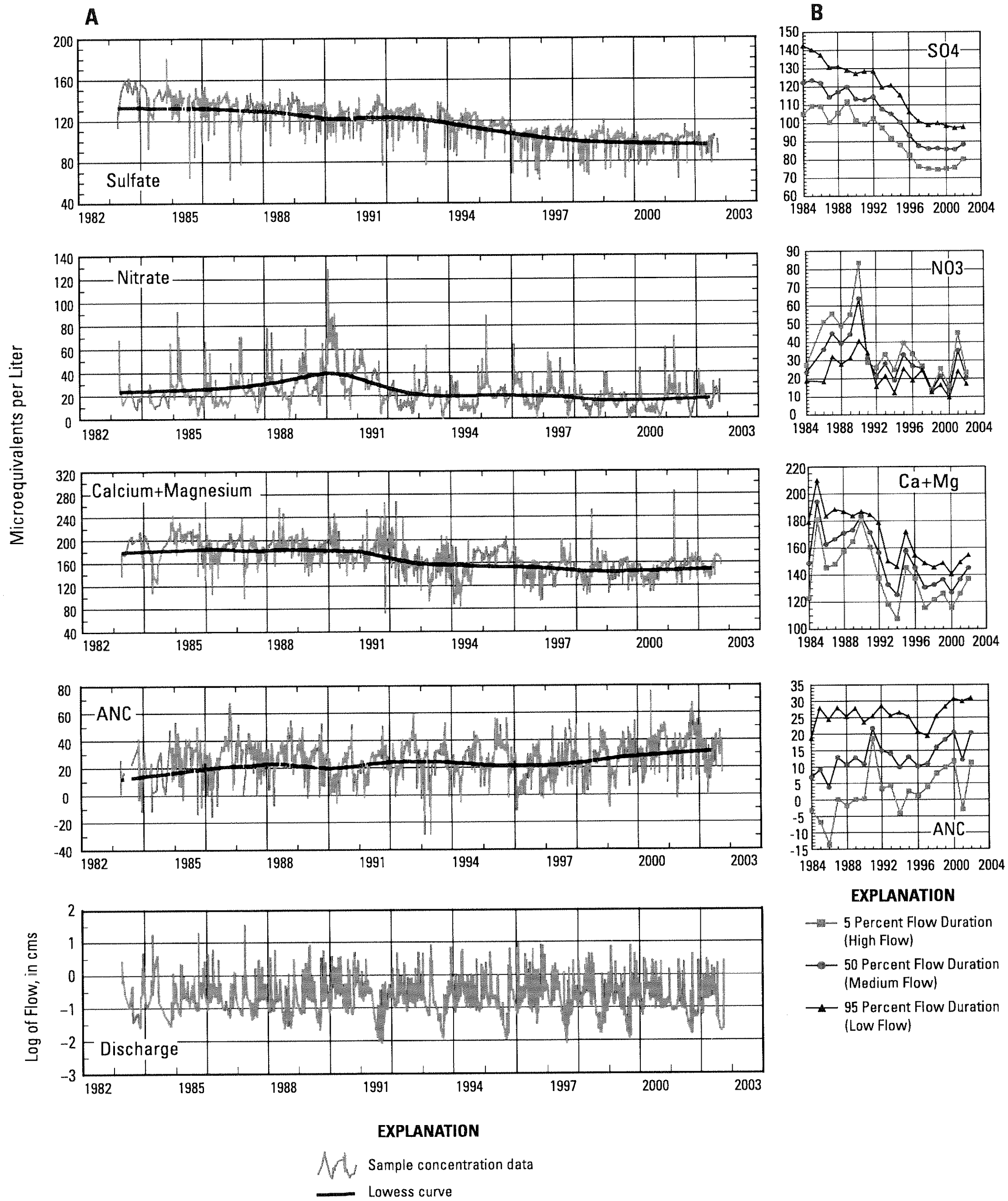

Figure 2. Temporal patterns in (a) concentrations of sulfate, nitrate, calcium plus magnesium, and acid-neutralizing capacity in Biscuit Brook and LOWESS estimate of average trend with temporal variation in discharge and (b) annual estimated concentrations of SO_4^{2-}, NO_3^-, Ca^{2+}+Mg^{2+}, and ANC at high, median, and low flows by water year at Biscuit Brook using segmented regression analysis (cms is cubic meters per second). See color version of this figure in the HTML.

flow levels; differences in slope indicate that the rate of change in water quality at high flow differed from that at median and low flow. The terms high, median, and low flow refer to the 5%, 50% and 95% flow duration levels, respectively.

2.3.3. Criterion 3: Scientific Consistency

[26] No current trend analysis method provides trend detection at specific flow conditions, and thus a direct assessment of the validity of the SRA annual segment results at high, medium, and low flow was not feasible. However, qualitative assessments of the direction and magnitude of change over time can be made through comparing the results to observed solute concentration patterns in stream water, soil water, and atmospheric deposition. A locally weighted scatterplot smoothing (LOWESS) curve (15% span) was applied to a plot of sample concentration of each constituent versus time to allow a visual assessment of major patterns in concentration for the period

Table 1. Trends in Stream Chemistry in Biscuit Brook for the Period of Record (WY84–WY02) Determined by Flow-Adjusted Seasonal Kendall Tau (SKT), Multiple Regression Residual Analysis (MRRA), and Segmented Regression Analysis (SRA)[a]

Method	Constituents			
	SO_4^{2-}	NO_3^-	ANC	Ca^{2+}+Mg^{2+}
SKT	−2.54	−0.56	0.45	−2.91
MRRA	−2.65	NS	NS	−3.02
SRA-5% (high flow)	−2.76	−0.69	−0.22	−3.06
SRA-50%	−2.48	−1.19	0.50	−2.56
SRA-95% (low flow)	−2.24	−1.62	0.74	−2.15
EPA survey	−2.27	−1.37	0.79	NA

[a]Units are microequivalents per liter per year. ANC is acid-neutralizing capacity; NS means not significant at $p < 0.01$; NA means not analyzed; SRA-5% represents the trend slope for concentrations at 5% flow duration, etc.; and EPA survey refers to 11-year (1990–2000) assessment for northeastern streams at base flow [*Stoddard et al.*, 2003].

of record [*Helsel and Hirsch*, 1992] (Figure 2). Average annual concentrations and loads of each constituent in deposition were plotted against time and compared to the timelines of SRA-determined concentrations. Soil water samples collected biweekly to monthly provided a third point of reference for assessing inflections in the long-term trends provided by the SRA.

[27] The minimum length of record recommended for an SKT trend test is 8 years [*Helsel and Hirsch*, 1992]. However, changes in trend between two overlapping periods of time at an individual stream, in which both periods have more than 8 years of record, can be used to assess changes in trend between the ending years of each period assessed (R. Alexander, USGS, oral communication, 2004). This "incremental" trend test was applied to the deposition and stream data, to compare solute trends for the period WY84–WY96 to the full 19 years of record (WY84–WY02).

3. Results

[28] LOWESS curves of SO_4^{2-} and Ca^{2+}+Mg^{2+} in stream water indicate a general decrease in concentration since 1984, but showed short periods of diminished concentration trends during that time, and the slope of the negative trend flattened in the last 6 years of record (Figure 2a). NO_3^- concentrations increased from a low in WY84 to a peak in WY90, then declined sharply in WY91 and remained low thereafter. ANC showed a slight visible upward trend over the period of record, most apparent since 1997. An important consideration when interpreting trends is that SO_4^{2-}, ANC, and Ca^{2+}+Mg^{2+} concentrations decrease with increasing discharge whereas NO_3^- concentrations generally increase with increasing discharge at this site.

3.1. Criterion 1: Concentration Trends Determined by Multiple Methods

[29] Period of record trends of SO_4^{2-}, ANC, and Ca^{2+}+Mg^{2+} concentrations determined using SRA for high-, medium-, and low-flow conditions spanned a range that was similar to those determined by SKT and MRRA methods, and the general visible patterns provided by the LOWESS analysis (Table 1 and Figures 2a and 2b). The medium-flow SRA trend (SRA-50) was similar in magnitude to the trend predicted by the SKT analysis, thus validating the SRA method. MRRA trend slopes were slightly higher than the SRA-50% trends, but still less than the high-flow SRA (SRA-5) trend. The SRA-50 trend for ANC was similar to the SKT trend, and the SRA-95 (low-flow) trend approximated regional ANC trends reported by EPA (EPA trends from 1990–2000 assessment of Northeastern streams at base flow [*Stoddard et al.*, 2003]). The SKT trend for NO_3^- was most similar to the SRA-5 trend, which is consistent with the observation that NO_3^- concentrations changed at high flow but not at low flow. The regional base flow trends for NO_3^- from the EPA assessment were between the rates of the SRA-50 and SRA-95 [*Stoddard et al.*, 2003]. The NO_3^- trends by MRRA were not significant; residuals of the concentration-to-discharge model for NO_3^- using MRRA show a temporal pattern that indicates that the model does not capture all factors that control NO_3^- concentrations in stream water. However, with the exception of the MRRA trend for NO_3^-, criterion 1 was generally met by the SRA analysis.

3.2. Criterion 2: ANCOVA Comparison of Flow-Specific Trends by SRA

[30] The C-Q regressions derived from segmenting the data into three sequential periods (WY85–WY90, WY91–WY96, and WY97-WY02) using SRA indicated that significant changes in concentration trend can occur at one flow duration level but not at another (Figure 3 and Table 2). The ANCOVA test indicated that a relatively consistent decrease in SO_4^{2-} and Ca^{2+}+Mg^{2+}concentrations occurred over the entire flow range during the period of record, but changes in concentration of ANC and NO_3^- were significantly greater at high flow than at low flow. The changes in NO_3^- concentrations between the second and third segments (WY91–WY96 and WY97–WY02) were consistent across the range of flows, and increases in ANC for the same period were also consistent and minor (Figure 3). Episodic acidification by NO_3^- had therefore diminished significantly after WY90.

3.3. Significance of Annual C-Q Relationships

[31] Annual concentration-discharge regressions using SRA were significant ($p < 0.01$) for SO_4^{2-}, NO_3^-, Ca^{2+}+Mg^{2+}, and ANC for each year of the record at Biscuit Brook. Trends in stream discharge and deposition volume as determined by SKT were not significant for the period of record ($p < 0.05$; Table 3). Trends in stream water quality are therefore not explained by trends in flow or precipitation amount. Assessing changes in the slope or standard deviation (SD) of annual C-Q regressions over time may be useful for early detection of changes in stream chemistry. For example, both the slope and SD of the annual relationship between NO_3^- and stream discharge diminished rapidly in WY91 and have been relatively stable since (Figure 4). In contrast, the SD of the relationship between Ca^{2+}+Mg^{2+} concentrations and discharge became much more variable in WY91. Annual slopes and SDs of the C-Q relations for SO_4^{2-} and ANC concentrations showed much less interannual variability ($p < 0.05$). The standard deviation (SD) for annual C-Q regressions of SO_4^{2-} and NO_3^- concentrations decreased over the period of record ($p < 0.05$; Figure 4),

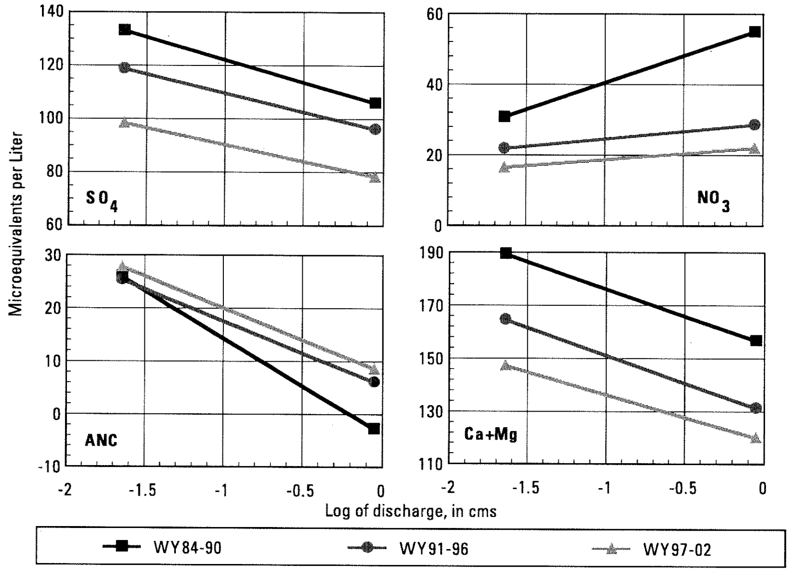

Figure 3. Relation of SO_4^{2-}, NO_3^-, Ca^{2+}+Mg^{2+}, and ANC concentrations to discharge for 6-year segments of data from Biscuit Brook, New York (cms is cubic meters per second). See color version of this figure in the HTML.

implying a decrease in the magnitude of episodic changes in concentration. The annual C-Q relationships of ANC and Ca^{2+}+Mg^{2+} showed no significant trend in SDs over time ($p < 0.05$).

3.4. Criterion 3: Consistency of Annual SRA Trends With Hydrologic and Deposition Conditions

[32] Estimated annual concentrations of SO_4^{2-}, NO_3^-, Ca^{2+}+Mg^{2+}, and ANC indicate differences in both within-year concentration and multiyear trends at the 5%, 50%, and 95% flow duration levels. Those differences were consistent with the hydrologic characteristics and atmospheric deposition trends of the Biscuit Brook watershed (Figure 2b). These are briefly described for each constituent below.

3.4.1. Sulfate

[33] SO_4^{2-} concentrations exhibited a significant ($p < 0.001$) decreasing trend over the period of record in all flow classes, but the magnitude of the trend varied by flow duration level (Table 1). Flow-specific SO_4^{2-} concentrations were lower at high flow (5% duration) than at low flow (95% duration) for the entire period of record, consistent with the previously observed inverse relation between concentration and flow. The downward trend at low flow became less steep after WY97, whereas the trend at median flow (50% duration) was flat after WY97, and the average concentration at high flow increased each year after a low in WY98 (Figure 2b). The rate of decline in SO_4^{2-} deposition also diminished between WY96 and WY02, consistent with flattening of the annual SRA trends for stream water (Table 3). SO_4^{2-} concentrations in deposition decreased sharply during WY95, coinciding with low rainfall volumes and the large emission reductions associated with the implementation of the CAAA, but increased to pre-WY95 levels in WY00 despite large increases in precipitation amount (Figure 5). SO_4^{2-} concentrations declined in *B* horizon soil solutions collected near Biscuit Brook through 1998, then increased through 2002, paralleling the observed changes in high-flow stream water and precipitation concentrations (Figure 6).

3.4.2. Nitrate

[34] NO_3^- concentrations in all three flow classes peaked in WY90 in association with extreme winter temperatures, frozen soils, and high winter NO_3^- deposition [*Mitchell et al.*, 1996; *Murdoch et al.*, 1998], then declined thereafter at rates that differed among the flow classes (Figures 2b and 3). Average NO_3^- concentrations at high flow declined by more than 50 μeq/L during WY91, and continued to gradually decline to a low of 16 μeq/L in WY00. NO_3^- concentrations at low flow peaked in WY90, then declined by about 25 μeq/L through WY92 and remained low thereafter (Figure 2b). Concentrations at high and median flows were much higher in WY01 than in WY00, the highest NO_3^- deposition year, but those at low flow were only slightly higher in WY01 than in WY00. NO_3^- concentrations were higher at high flows than at low flows except during WY91 (Figure 2b). No SKT trend in NO_3^- or NH_4^+ deposition was present for the period of record (Table 3). NH_4^+ is negligible in stream water, but

Table 2. Significance of Differences in Slope and Intercept of Concentration-Discharge Relationships in Biscuit Brook, New York, for the Periods WY84–WY90 and WY97–WY02 Compared to the Period WY91–WY96 Using a Three-Way ANCOVA Test[a]

	1984–1990		1997–2002	
Constituent	Slope	Intercept	Slope	Intercept
SO_4	X	X		X
NO_3	X	X		X
ANC	X	X		
Ca+Mg		X		X

[a]X indicates significant, and blanks indicate nonsignificant.

Table 3. Trends in Sen Slope Estimators for Precipitation Amount and Chemistry at Station NY68, Biscuit Brook, Ulster County, New York, Based on Seasonal Kendall Tau Analysis[a]

Dates	Precipitation Amount	p	Constituent SO_4^{2-}	p	NO_3^-	p	NH_4	p	Ca+ Mg	p	H	p
1984–1996	0.07	0.46	−1.05	0.002	−0.05	0.660	0	1.00	−0.20	0.001	−0.75	0.190
1984–2002	0.02	0.74	−0.87	<0.001	−0.13	0.370	0.04	0.68	−0.10	0.001	−0.73	0.005

[a]Units are microequivalents per liter per year. Location is shown in Figure 1.

makes up a significant portion of the total nitrogen (N) in deposition.

3.4.3. Calcium Plus Magnesium

[35] Ca^{2+}+Mg^{2+} concentrations at high and median flows reached a maximum in the early 1990s, then declined to a low in WY94 and have increased slightly but erratically thereafter (Figure 2b). Low-flow concentrations were stable or gently declining during the late 1980s and early 1990s, but declined rapidly (approximately 30 μeq/L) in the mid-1990s before stabilizing at the lower concentration after WY96 (Figure 2b). Ca^{2+}+Mg^{2+} concentration showed a slight but significant downward trend (p = 0.001) in deposition, and a significant decrease in hydrogen ion concentration was also indicated over the period of record (Table 3). The trend of decreasing Ca^{2+}+Mg^{2+} and hydrogen ion concentrations roughly balanced the observed trend in deposition SO_4^{2-} concentration.

3.4.4. Acid-Neutralizing Capacity

[36] Trends in ANC concentrations at high and median flow were generally upward throughout the record, although the rate of change increased after WY96. In contrast, ANC concentrations at low flows increased during the 1980s, decreased from WY90 to WY97, and increased again after WY97. The reversal of the low-flow ANC trend after WY97 occurred 2 years after the sharp decrease in SO_4^{2-} deposition at Biscuit Brook (Figure 2b).

4. Discussion

[37] The similarity among the period-of-record trends determined by three very different approaches to trend detection indicates that our first criterion for method validation was met. The simple regression approach of the SRA method is generally consistent with other established methods, and provides an alternative that allows separate determination of trends at any specified flow condition.

[38] The results of the ANCOVA test supported our second criterion for method development. Statistically significant differences in the slope and intercept of the 6-year C-Q regression models confirmed that changes in concentration can be significantly different at high flow than at median or low flow, and these differences are consistent with our understanding of watershed hydrology at Biscuit Brook (Criterion 3). This difference between concentration trends that occur in high flows, which reflect the chemical quality of recent deposition and shallow soil water (short residence time waters), and those that occur at low flows, which reflect the chemical quality of groundwater affected by deposition that entered the system months or years earlier (long residence time waters), suggests that the high-flow concentration trends could provide an early indication of stream response to changes in climate or deposition chemistry. Differences in the standard deviations of the C-Q relations from year to year also provide valuable information, in this case showing a reduction in the annual variability of SO_4^{2-}, NO_3^-, and Ca^{2+}+Mg^{2+} concentrations over time. The results of the SRA of Biscuit Brook indicate that since 1990 concentrations of all constituents measured have changed more at high flow than at low flow, but NO_3^- had the greatest change in the slope of the C-Q relationship. The recovery of ANC concentrations in Biscuit Brook as a result of decreased industrial emissions of sulfur and nitrogen will therefore be detectable sooner by a high-flow trend analysis than by standard methods of trend detection.

[39] Results of the annual segment SRA for Biscuit Brook were consistent with our current understanding of the processes that control the effects of acid deposition on streams. Changes in SO_4^{2-} and NO_3^- deposition rates affect the concentrations of these solutes on the watershed surface and in shallow soils sooner than in deeper flow paths, and these near-surface processes (nitrate leaching; sulfate adsorption/desorption) will be reflected sooner in the surface runoff and shallow soil water that contribute to stormflow than in the deeper groundwater that supplies base flow. The long-term decline in deposition SO_4^{2-} concentrations was reflected in relatively gradual trends in SO_4^{2-} concentrations across the range of flows. The SO_4^{2-} concentrations in the last 6 years of record (WY97–WY02) at Biscuit Brook indicate a flattening of concentration trends, followed by reversal of the long-term trend, but that reversal was only evident at high flows. The stable rates of SO_4^{2-} deposition at the NADP station from WY96 to WY99, and the increased

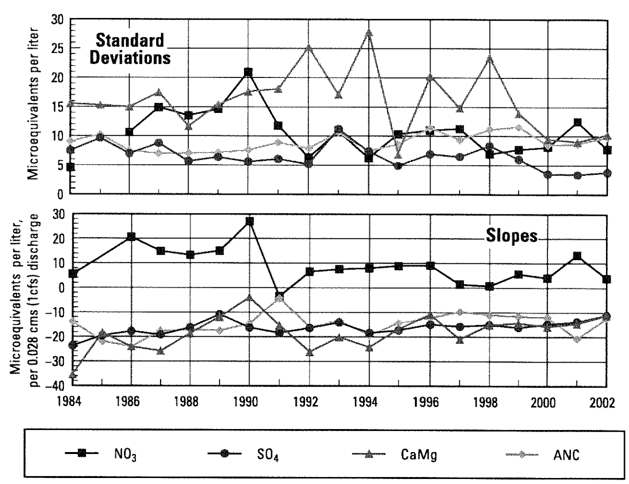

Figure 4. Temporal patterns in the slope and standard deviation of annual concentration-discharge relationships determined for Biscuit Brook, New York. See color version of this figure in the HTML.

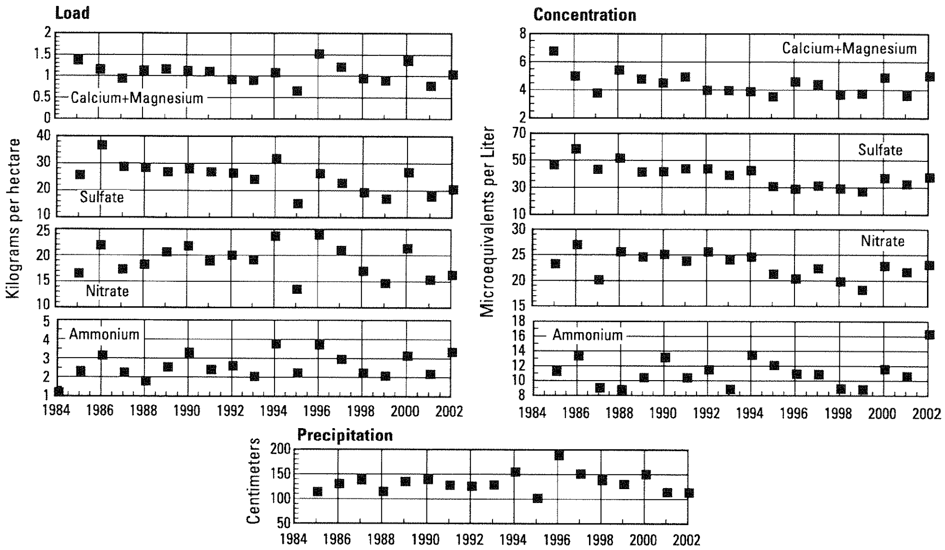

Figure 5. Average annual loads and concentrations of Ca^{2+}+Mg^{2+}, SO_4^{2-}, NO_3^-, and NH_4^{2+} in deposition and deposition volume at the National Trends Network precipitation monitoring station at Biscuit Brook, New York, for water years 1984–2002.

deposition rate in WY00 correlate with stable SO_4^{2-} concentrations in the stream during WY96–WY99 and increased SO_4^{2-} concentrations at high flow in WY00–WY02, both periods in which base flow trends in SO_4^{2-} concentrations continued downward. The supporting evidence of increasing SO_4^{2-} concentrations in soil solutions during WY00–WY02 adds further credence to the observed reversal of the SO_4^{2-} high-flow trends in stream water indicated by the SRA. Sulfate budgets for the Biscuit Brook watershed are roughly balanced between deposition load and stream flux [*Murdoch*, 1991], indicating little retention in watershed soils, and sulfate in stream water consistently decreases with increasing discharge. Increased stream and soil water concentrations in WY01–WY02 can be partly explained by the concentrating effect of low precipitation in those years. If deposition loads are constant, however, increased precipitation should result in a dilution of SO_4^{2-} concentrations in soil water, yet soil water SO_4^{2-} concentrations increased despite wetter than normal conditions in WY00, reflecting the higher SO_4^{2-} load in deposition that year (Figure 6).

[40] The SRA also suggests that high-flow concentrations of ANC have been generally increasing since WY84, but concentrations at the lowest flows (95% duration) declined from WY84 through WY96 and did not begin increasing until 2 years after the large reductions in emissions in WY95. The method therefore detects the response of stream water quality to changes in deposition quality sooner than would be possible with the SKT or MRRA methods.

[41] Previous studies have shown that trends in stream NO_3^- concentrations cannot be directly correlated with trends in N deposition because N deposition rates exceed the biological demand for N in the watershed [*Murdoch et al.*, 1998]. Other factors such as climate, pest infestation, etc., therefore control the annual and longer-term fluctuations in stream NO_3^- concentrations. However, the hydrologic controls of NO_3^- movement in the watershed still can cause important differences in concentration trends at different flows. The changes in the year-to-year NO_3^- C-Q relation indicated by the SRA support the conceptual model proposed by *Stoddard* [1994] for propagating N saturation through the hydrologic flow paths of a watershed. The high-flow trends of increasing stream water NO_3^- concentrations during the 1980s preceded increased NO_3^- concentrations in base flow during the years that followed, as the NO_3^- pulse moved from the shallow soil into groundwater and eventually discharged to the stream. Base flow concentrations rose more slowly than high-flow concentrations, and continued

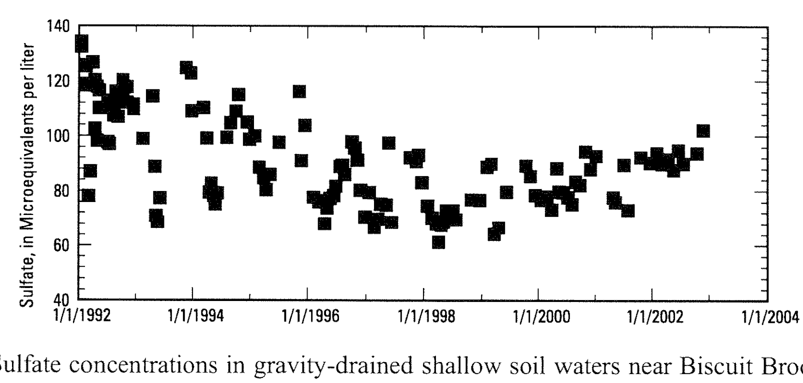

Figure 6. Sulfate concentrations in gravity-drained shallow soil waters near Biscuit Brook, New York, 1992–2002.

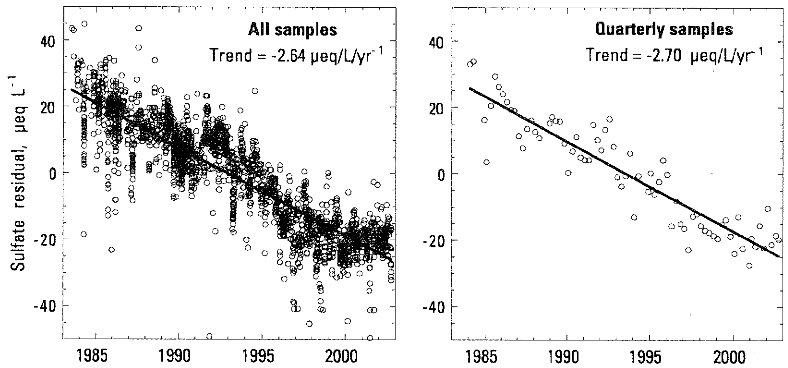

Figure 7. Comparison of trends in sulfate concentration at Biscuit Brook using (a) all available data and (b) one sample for each quarter-year period.

to reflect the WY90 peak concentrations through WY91. After WY91, base flow concentrations exhibited only minor decreases whereas high-flow concentrations dropped sharply. These differences in high- and low-flow response to climate are not discernible by the other methods of trend analysis.

4.1. Implications for the Effectiveness of the Clean Air Act Amendments

[42] A recent analysis of trends in deposition and stream water quality in the eastern United States from 1990 through 2000 [*Stoddard et al.*, 2003] indicated significant improvement in stream and lake ANC, and decreased SO_4^{2-} and NO_3^- concentrations in surface waters during the 10-year period. This trend analysis used linear regression of data collected infrequently from many streams to develop a regional trend estimate, and was not designed to consider high-flow or episodic changes in stream water quality. The trends reported are roughly consistent with the SRA median and low-flow trends for the same 10-year period (Table 1). The results received considerable attention as evidence that the CAAA strategies for curbing acid rain and its effects were having a beneficial effect. The incremental SKT and the SRA trends for Biscuit Brook suggest that the downward trend in SO_4^{2-} concentrations during 1990–2000 reported by *Stoddard et al.* [2003] has flattened since WY96 and possibly reversed from WY00 through WY02 at high flows, while the downward trend at low flows has remained more consistent with the 1990s trends. This change at high flow coincides with relatively constant SO_4^{2-} concentrations in deposition from WY95 through WY99, increases in deposition SO_4^{2-} concentrations and loads since WY99, and increases in SO_4^{2-} concentrations in shallow soil solution.

[43] National SO_4^{2-} emissions trends reported by *Stoddard et al.* [2003], *Lynch et al.* [2002], and *Environmental Protection Agency* [2002], indicate relatively stable emission levels from 1995–1998, followed by a 19% decline through 2002. Trends in sulfate concentrations in deposition and high-flow stream water at Biscuit Brook reflected the stable emission rates in the late 1990s, but deviated from emissions trends after 1999. The results of this study suggest that trends in local deposition in the Catskill Mountains may not always reflect the reported national emission trends, and illustrate the need for high-resolution methods such as SRA for separately tracking trends in surface water quality at high and low flow, particularly when national pollution management strategies are being assessed.

4.2. Sampling Requirements for Determining Trends Using SRA

[44] SRA requires a sufficient number of samples to be collected at a range of flows to define a significant C-Q relationship for each temporal segment. If a constituent of interest has a strong relationship with discharge, fewer samples will be required than if the relationship is weak. Fewer samples per year are required for multiyear segments than for single-year segments, with the implicit assumption that trends within a segment are minor in comparison to trends among segments. Using MRRA, we found that quarterly sampling (4 times per year) produced similar trends over 19 years to those developed on the entire Biscuit Brook data set (Figure 7). However, trend detection over shorter periods of record would require more frequent sampling, and the earliest detection of changes in surface water chemistry would require segmented C-Q relationships to be established. For new monitoring stations, establishing minimum-sampling strategies will initially require characterization of the C-Q relationship for the constituents of interest.

5. Conclusions

[45] The need to assess the effects of environmental legislation soon after that legislation has been enacted, and to identify and monitor the environmental indicators specific to that legislation, raises several questions for long-term environmental monitoring networks including which variables should be monitored, where the monitoring should be done, what types of data should be collected, and what quantity of data will be needed. Policymakers are often forced to wait long periods after pollution abatement strategies are in place to determine if the investment in those strategies yielded the desired results. Establishing and maintaining long-term networks for tracking basic ecosystem condition, and archiving samples for future analysis, can provide important background information for cost effective assessment and adjustment of management strategies, but responsiveness to the societal need for timely scientific information is an

essential component of any monitoring network that hopes to remain funded.

[46] The method of trend analysis presented here improves our ability to assess the effects of pollution mitigation strategies in a shorter timeframe than has been available to date. The SRA method should have immediate application to any stream with long-term water quality and discharge monitoring data, and will improve early detection of trends where it is applied. The initial application of SRA at Biscuit Brook indicates that a long-term trend (1984–2002) of decreasing high-flow SO_4^{2-} concentrations in surface waters accelerated during the mid-1990s, but leveled and possibly reversed during the period WY97–WY02. However, the comparatively rapid response of high-flow trends in stream chemistry to changes in deposition suggest that future reductions in nitrogen and sulfur deposition will result first in reduced concentrations of SO_4^{2-} and NO_3^- and increased ANC at high flow, and later by similar changes in base flow stream chemistry as the changes in deposition are transmitted through the watershed.

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