

## Long-term trends in stream water and precipitation chemistry at five headwater basins in the northeastern United States

David W. Clow and M. Alisa Mast

U.S. Geological Survey, Water Resources Division, Lakewood, Colorado

**Abstract.** Stream water data from five headwater basins in the northeastern United States covering water years 1968–1996 and precipitation data from eight nearby precipitation monitoring sites covering water years 1984–1996 were analyzed for temporal trends in chemistry using the nonparametric seasonal Kendall test. Concentrations of  $\text{SO}_4$  declined at three of five streams during 1968–1996 ( $p < 0.1$ ), and all of the streams exhibited downward trends in  $\text{SO}_4$  over the second half of the period (1984–1996). Concentrations of  $\text{SO}_4$  in precipitation declined at seven of eight sites from 1984 to 1996, and the magnitudes of the declines ( $-0.7$  to  $-2.0 \mu\text{eq L}^{-1} \text{yr}^{-1}$ ) generally were similar to those of stream water  $\text{SO}_4$ . These results indicate that changes in precipitation  $\text{SO}_4$  were of sufficient magnitude to account for changes in stream water  $\text{SO}_4$ . Concentrations of  $\text{Ca} + \text{Mg}$  declined at three of five streams and five of eight precipitation sites from 1984 to 1996. Precipitation acidity decreased at five of eight sites during the same period, but alkalinity increased in only one stream. In most cases the decreases in stream water  $\text{SO}_4$  were similar in magnitude to declines in stream water  $\text{Ca} + \text{Mg}$ , which is consistent with the theory of leaching by mobile acid anions in soils. In precipitation the magnitudes of  $\text{SO}_4$  declines were similar to those of hydrogen, and declines in  $\text{Ca} + \text{Mg}$  were much smaller. This indicates that recent decreases in  $\text{SO}_4$  deposition are now being reflected in reduced precipitation acidity. The lack of widespread increases in stream water alkalinity, despite the prevalence of downward trends in stream water  $\text{SO}_4$ , suggests that at most sites, increases in stream water  $\text{pH}$  and acid-neutralizing capacity may be delayed until higher soil base-saturation levels are achieved.

### 1. Introduction

#### 1.1. Background

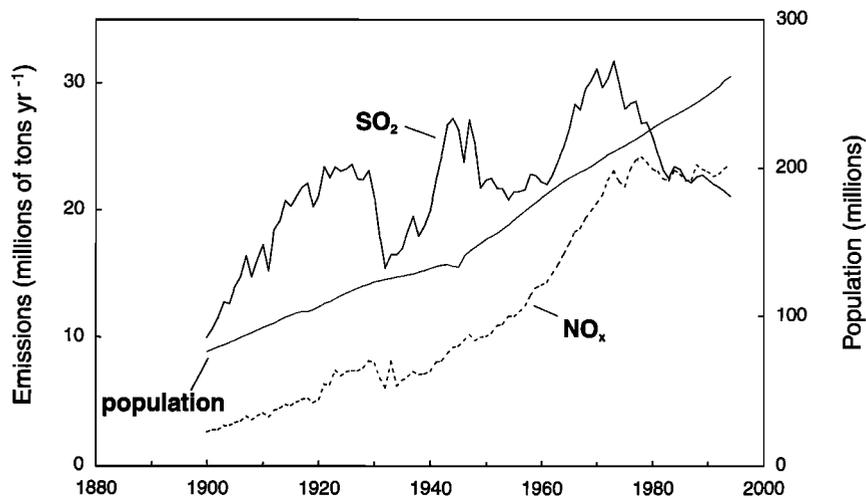
Ecosystems in the northeastern region of the United States have been subject to elevated levels of acidic deposition since the early part of the 20th century [Gschwandtner *et al.*, 1988]. The main components of acidic deposition are sulfuric and nitric acids, which are derived primarily from fossil fuel combustion. Historically, sulfuric acid has been more important than nitric acid as a source of precipitation acidity [Likens and Bormann, 1995], although the relative importance of nitric acid has increased substantially since 1970 [Gschwandtner *et al.*, 1988; Husar *et al.*, 1991]. Numerous studies have shown that soils and surface waters in many parts of the northeastern United States have been impacted by long-term exposure to acidic deposition [Stoddard, 1991; Murdoch and Stoddard, 1993; Likens and Bormann, 1995]. The most important effects of acidic deposition on soils are the mobilization of aluminum due to increased soil acidity and the leaching of base cations from the soil exchange complex [Ruess and Johnson, 1986; Wesselink *et al.*, 1995]. As base cations become depleted from the soil-exchange pool, the acid-neutralizing capacity (ANC) of streams and lakes declines and surface waters become more susceptible to episodic acidification during snowmelt and storm events [Stoddard and Murdoch, 1991; Driscoll and Van Dreason, 1993]. Depletion of cations, particularly Ca, from the soil exchange pool also has been implicated in the dieback of

red spruce forests in the northeastern United States [Shortle *et al.*, 1997].

Historical patterns in  $\text{SO}_2$  emissions rates indicate that although emissions have declined from their peak earlier this century, current emission levels are still much higher than during the preindustrial era. Regional and national emissions data summarized by Husar *et al.* [1991] and Nizich *et al.* [1995] indicate that  $\text{SO}_2$  emissions in the northeast and in the United States as a whole rose substantially during the early part of the 20th century and have fluctuated since then, with increasingly larger peaks in the 1920s, 1940s, and 1970s (Figure 1). Emissions of  $\text{SO}_2$  declined by one third between 1970 and 1994, mostly owing to the combined effects of economic recessions in the mid to late 1970s and early 1990s and emissions controls mandated by the Clean Air Act of 1970 [Nizich *et al.*, 1995]. Clean Air Act amendments enacted in 1990 specified further reductions in  $\text{SO}_2$  emissions, which were reflected in substantial declines in  $\text{SO}_2$  output in 1995, the first year of compliance [Lynch and Bowersox, 1996]. Emissions of  $\text{NO}_x$  in the northeast rose steadily during the 20th century until the 1970s, when they leveled off (Figure 1). The overall decline in emissions of acid precursors ( $\text{SO}_2 + \text{NO}_x$ ) over the past two decades has led to a decrease in strong-acid anion deposition during that period [Lynch *et al.*, 1995b, 1996]. It might be expected that at some point soils and aquatic ecosystems should begin to recover from their long-term exposure to acidic deposition. Conceptual ecosystem acidification models predict that surface waters will respond to reduced sulfuric acid deposition with higher  $\text{pH}$  and alkalinity and lower concentrations of  $\text{SO}_4$  and base cations [Galloway *et al.*, 1983; Ruess and Johnson, 1986]. Given the

This paper is not subject to U.S. copyright. Published in 1999 by the American Geophysical Union.

Paper number 1998WR900050.



**Figure 1.** Trends in population, SO<sub>2</sub>, and NO<sub>x</sub> emissions in the United States for the period 1900–1995 [Nizich *et al.*, 1995].

high economic cost of pollution controls, it would be useful to evaluate whether the responses predicted by the conceptual models have occurred and whether the emissions reductions have been of a magnitude sufficient to achieve the desired result (i.e., reversal of ecosystem acidification).

Data from Hubbard Brook, New Hampshire, suggest that concentrations of SO<sub>4</sub> and base cations in stream water have decreased in response to declining atmospheric deposition, but stream pH at Hubbard Brook has been relatively invariant and ANC has remained negative [Driscoll *et al.*, 1989; Likens *et al.*, 1996]. It is uncertain whether the stream water response seen at Hubbard Brook is a regional phenomenon. Data from the U.S. Environmental Protection Agency's Long-Term Monitoring program indicate that during the 1980s, SO<sub>4</sub> concentrations declined in surface water in the northeast, but trends in base cations and alkalinity were not consistent across the region [Driscoll and Van Dreason, 1993; Kahl *et al.*, 1993; Murdoch and Stoddard, 1993; Stoddard and Kellogg, 1993]. Stream water data collected between the mid-1960s and the early 1980s through the Hydrologic Benchmark Network (HBN), a national network of small, mostly undisturbed basins operated by the U.S. Geological Survey (USGS), indicated declining SO<sub>4</sub> concentrations at stream sites in Maine and New York but no significant changes in SO<sub>4</sub> at other sites in the northeast [Smith and Alexander, 1983; Kramer *et al.*, 1986]. Trend analyses on the HBN data collected since the early 1980s have not been reported, but the continued decline in SO<sub>4</sub> deposition in the northeast suggests that a new analysis of the HBN data is warranted.

## 1.2. Purpose and Scope

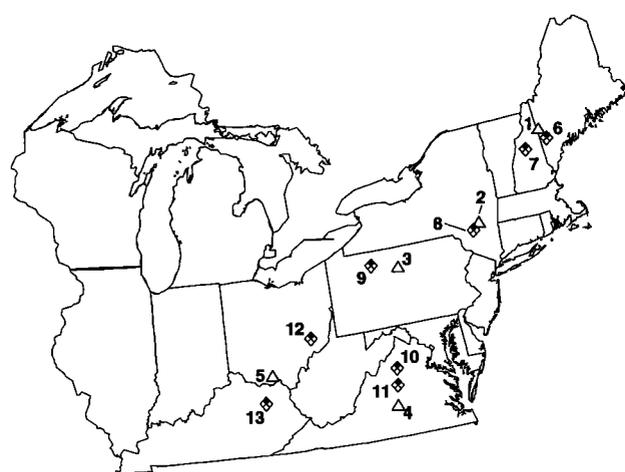
The purpose of this study was to test for trends in stream water chemistry at five HBN sites in the northeastern United States over the period 1968–1996 and to evaluate possible cause(s) for any observed trends. The HBN data set has extended another 15 years since the initial trend analyses of Smith and Alexander [1983] and Kramer *et al.* [1986], and it now covers the period during which high-quality precipitation chemistry data are available for comparison. Attention was focused on HBN sites in the northeast because the area historically has had the highest acidic deposition rate in the nation

(in this paper the upper Ohio River Valley is considered part of the northeast region).

Stream water chemistry data were tested for trends over the period of record during which all five HBN sites were operating (1968–1996) and over two shorter periods, 1968–1983 and 1984–1996. Tests on the shorter-term records allowed comparisons with (1) results of previous trend analyses on HBN stream water chemistry for the 1968–1983 period and (2) results of trend analyses on precipitation chemistry for the 1984–1996 period, performed as part of the present study. Possible causes for trends in stream water chemistry that were investigated included potential linkages between trends in stream water chemistry and precipitation chemistry, changes in analytical methodology, and changes in land use in the study basins. This paper focuses on trends in SO<sub>4</sub>, Ca + Mg, and alkalinity in stream water; SO<sub>4</sub>, Ca + Mg, and H in precipitation; and stream discharge and precipitation volumes. These chemical constituents probably are the main solutes driving the long-term acid/base status of surface waters in the study basins. Several recent studies of small basins in the northeast region of the United States have indicated that nitrogen compounds may be becoming an increasingly important source of acidity to precipitation and stream water [Murdoch and Stoddard, 1993; Stoddard, 1991]. However, nitrate concentrations at the HBN sites used in this study generally were near the analytical detection limit and exhibited no significant trends. Lower nitrate concentrations are expected in the HBN basins because flow paths are longer and soils are more extensive in these comparatively large basins. Because there were no trends in nitrate in stream water and only one weak trend in precipitation nitrate, nitrogen compounds are not discussed further in this paper. Other major constituents were tested for trends, but the results are not presented here unless they affect the interpretation of trends in SO<sub>4</sub>, Ca + Mg, alkalinity, or H. Ca and Mg were considered together because of their similar geochemical behavior and because they usually were the dominant cations in stream water.

## 1.3. Basin Characteristics

The HBN was established in the 1960s as a national stream-flow and water-quality monitoring network designed to docu-



- HBN STATIONS  $\triangle$
- 1 Wild River, ME
  - 2 Esopus Creek, NY
  - 3 Young Womans Creek, PA
  - 4 Holiday Creek, VA
  - 5 Upper Twin Creek, OH
- NADP STATIONS  $\diamond$
- 6 Bridgeton, ME
  - 7 Hubbard Brook, NH
  - 8 Biscuit Brook, NY
  - 9 Kane Experimental Forest, PA
  - 10 Shenandoah National Park, VA
  - 11 Charlottesville, VA
  - 12 Caldwell, OH
  - 13 Clark State Fish Hatchery, KY

**Figure 2.** Locations of selected Hydrologic Benchmark Network and National Atmospheric Deposition Network stations in the northeastern United States.

ment hydrologic characteristics at sites minimally impacted by human activities [Cobb and Bieseker, 1971; Lawrence, 1987]. Data collection has included continuous discharge measurements at permanent gauges, and periodic samples were taken at the gauges for water quality, with frequencies that generally ranged from monthly to quarterly. One of the original uses identified for the data was to study long-term trends in stream-

flow and stream chemistry and their possible relations to changes in atmospheric deposition.

The HBN sites used in this study are the Wild River in Maine, Esopus Creek in New York, Young Womans Creek in Pennsylvania, Holiday Creek in Virginia, and Upper Twin Creek in Ohio (Figure 2). Site characteristics and stream water chemistry have been summarized by Mast and Turk [1998], and hydrologic characteristics have been summarized by Lawrence [1987] (Table 1). All of the study sites are headwater basins that drain predominantly undeveloped forested areas, although logging has occurred at all of the sites in the past. Glaciers scoured the two northernmost drainages, Wild River and Esopus Creek, during the late Pleistocene and deposited till of varying thickness. The other study sites are unglaciated and lie beyond the southern limit of the Wisconsin glaciation. Soils at all of the sites are well drained and acidic, with low base saturation, and all except the Holiday Creek soils have low sulfate-adsorption capacities. Stream water chemistry largely reflects the interaction of acidic precipitation with the local soils and bedrock. Stream water sulfate exceeds or is nearly equivalent to bicarbonate at all of the sites except Holiday Creek, where atmospheric sulfate appears to be retained in basin soils. None of the streams are chronically acidic at the basin outlets; however, episodic acidification in tributaries to the Wild River and in high-order streams near Esopus Creek has been documented during storm events [Murdoch and Stoddard, 1993; Mast and Turk, 1998].

## 2. Methods

### 2.1. Data Sources

The stream water data set consists of stream water chemistry and instantaneous discharge measurements at five HBN streams in the northeastern United States for October 1967 through September 1996. These dates correspond to water years 1968–1996; the convention used in this paper when discussing trend results is to use water years, which begin in October and end in September. Analytical methods used by the USGS laboratories are documented by Fishman and Friedman [1989] and Fishman et al. [1994]. Quarterly volume-weighted mean concentrations in precipitation were obtained from the National Atmospheric Deposition Program (NADP) for eight precipitation-monitoring sites located near the HBN

**Table 1.** Site Characteristics of Hydrologic Benchmark Network Study Sites in Northeastern United States

Study Site	Basin Size, km <sup>2</sup>	Elevation, m	Soil	Geology	Average Annual Precipitation, cm	Average Annual Runoff, cm
Wild River, Maine	180	213–1478	highly acidic spodosols developed on Pleistocene till	glaciated; gneiss, mica schist, quartzite, glacial till	120	88
Esopus Creek, N. Y.	154	310–1145	acidic inceptisols developed on Pleistocene till	glaciated; shale, sandstone, conglomerates, glacial till	130	80
Young Womans Creek, Pa.	120	240–665	extremely acidic inceptisols formed from local bedrock	unglaciated; sandstone, siltstone, shale, conglomerate, limestone	105	55
Holiday Creek, Va.	22	145–280	extremely acidic loam and gravelly silty loam	unglaciated; phyllite, schist, amphibole gneiss and schist	106	37
Upper Twin Creek, Ohio	31.6	164–395	acidic Ultisols formed from local bedrock	unglaciated; sandstone, siltstone and shale, locally calcareous and carbonaceous	105	38

basins [NADP, 1984–1996]. Data records were obtained for each NADP site from the time of station startup through water year 1996; start-up dates ranged from 1978 to 1984. Volume-weighted mean concentrations were calculated by the NADP from weekly concentration and volume data as described in the NADP annual data summaries [NADP, 1984–1996]. Collection and analytical methods used by the NADP are described by Peden [1983].

## 2.2. Data Screening

Prior to trend analyses, the stream water data were examined for outliers and possible periods of analytical bias. As with any historical water-quality data set, methods-related changes have the potential to affect the results of trend analyses and can lead investigators to identify trends when in fact none exist or to mask trends that do exist. Stream water data were screened using two initial criteria: (1) ion imbalances greater than  $\pm 20\%$ , calculated as the total cationic charge minus the total anionic charge divided by the total charge in solution, and (2) identification of extreme outliers in a matrix of solute-solute plots. For samples where ion imbalances exceeded  $\pm 20\%$ , the solute-solute plots usually were helpful in identifying which solutes appeared to be in error, and analytical results for those solutes were excluded from the data set. If no single solute or group of solutes could be identified as being responsible for causing the large charge imbalances, analytical results for the entire sample were excluded. Time series plots of stream water concentrations were inspected visually for step functions, which can indicate changes in analytical bias due to methods changes. The USGS central laboratory has routinely incorporated blind-audit samples into each analytical run since the early 1980s, and the results are reported by the USGS Branch of Quality Assurance [Ludtke and Woodworth, 1997]. The bias of results for blind-audit samples analyzed by the central laboratory between 1985 and 1996 were tested for trends and inspected for step functions.

Analytical bias appeared to affect the stream water  $\text{SO}_4$  record during two periods. A positive bias was identified by a step function in stream water  $\text{SO}_4$  results between April 1986 and June 1989, and the problem was traced to the omission of a background sample-absorbance adjustment when using the turbidimetric analysis procedure [Schertz *et al.*, 1994]. The amount of bias largely depended on the sample matrix and color of the samples. Adjusted and unadjusted  $\text{SO}_4$  values were reported by the laboratory from July 1989 through March 1990, which permitted calculation of a correction factor that was applied to  $\text{SO}_4$  values reported between April 1986 and June 1989. Because the magnitude of bias depended on the sample matrix and color, separate correction factors were applied to data from each site. The turbidimetric method was replaced by an improved method (ion chromatography) in April 1990.

Time series plots of bias in the blind-audit data indicated that  $\text{SO}_4$  concentrations were biased low by about  $10 \mu\text{eq L}^{-1}$  from January 1995 through mid 1996. Although the cause of the bias was not identified, a correction factor was derived by regressing the measured concentration against the “known” concentration of the blind-audit samples ( $r^2 = 0.996$ ,  $n = 60$ ). The correction factor was applied to stream water samples analyzed in 1995 and the first half of 1996. Trend tests on the blind-audit samples prior to adjustment indicated a significant downward trend in the data ( $p < 0.001$ ), whereas after adjustment there was no trend ( $p > 0.5$ ). Trend tests on

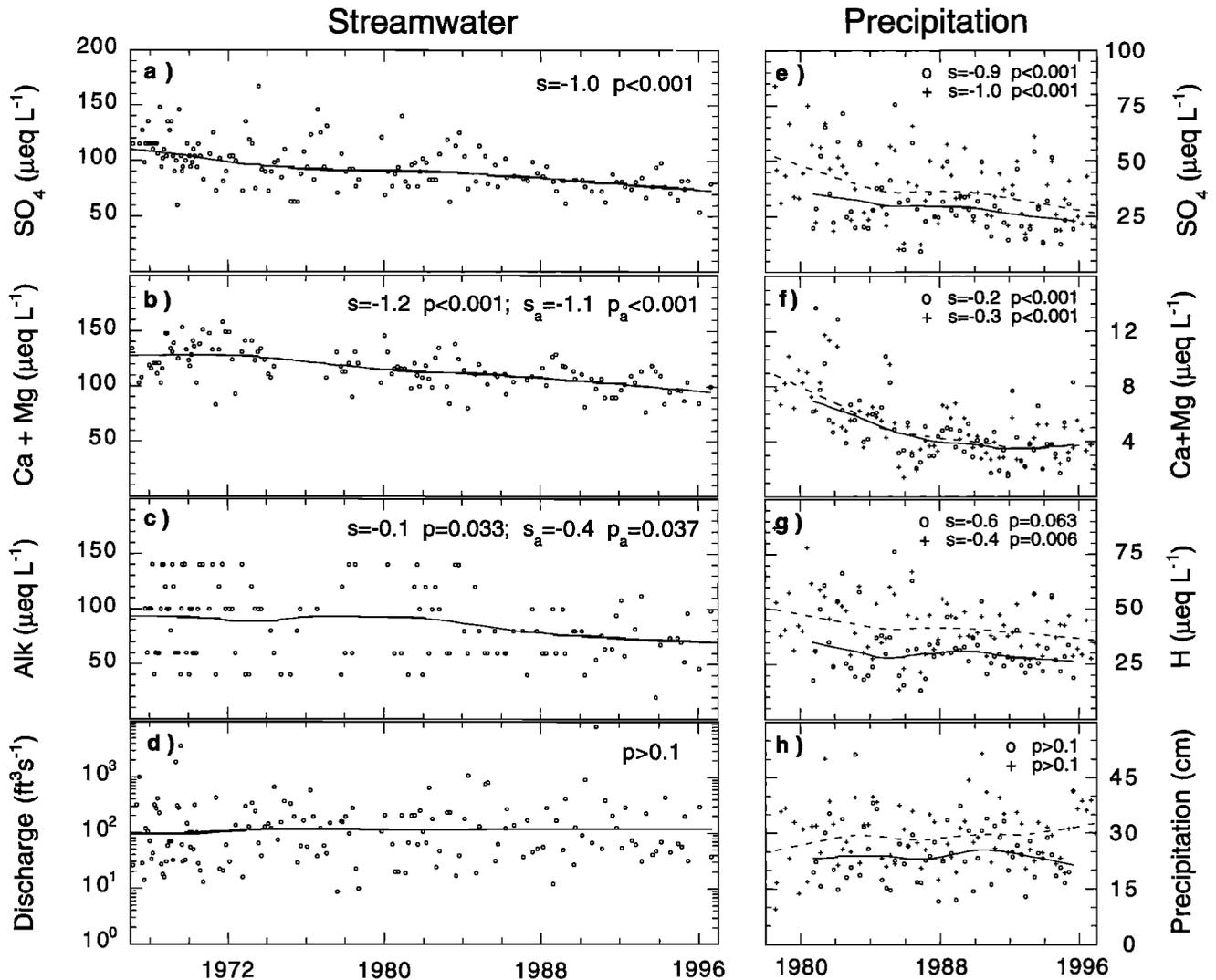
blind-audit results for other constituents discussed in this paper indicated no significant methods-related trends for 1985–1996 at  $p < 0.1$ . The effect of the biases and the bias corrections are presented in more detail in the Discussion.

Precipitation data analyzed by the NADP are checked internally using criteria based on rain gauge depth, sample volume, sampling interval, and availability of quality-assured analytical results. Data meeting the established criteria, which are described in the NADP annual data summaries [NADP, 1984–1996], are considered valid samples and are uploaded into the NADP database. The NADP program has established data completeness criteria for calculating quarterly volume-weighted mean concentrations to provide a measure of whether the available data are adequate to characterize the summary period. The criteria include having a minimum number of valid samples for the period and having a minimum percentage of total precipitation during the period represented by valid samples [NADP, 1984–1996].

## 2.3. Statistical Analyses

Stream water-chemistry and precipitation-chemistry data were tested for temporal trends using the seasonal Kendall test (SKT), which is a nonparametric test that is well suited for analyzing temporal trends in seasonally varying water-quality data [Hirsch *et al.*, 1982]. The SKT tests for monotonic trends, that is, whether there has been a statistically significant change in concentration over time. No assumptions are made about linearity of trends or normality of the data, and because the test is nonparametric, it is insensitive to the presence of outliers and missing values. The SKT accounts for seasonality by testing for trends in each season separately and then combining the results [Schertz *et al.*, 1991]. The test can be applied to raw concentration data as well as flow- or volume-adjusted data, which permits one to account for the variance in chemistry attributable to variations in discharge or precipitation amount. This feature is important because solutes in stream water often show a strong correlation with discharge. Flow- and volume-adjusted concentrations were calculated using regression models of the form  $f(Q) = \ln Q$  or  $f(Q) = 1/(1 + BQ)$ , where  $Q$  is instantaneous discharge and  $B$  is one of eight coefficients scaled according to the observed range of discharge [Schertz *et al.*, 1991]. Flow-adjusted concentrations associated with the “best” model, selected on the basis of which model provided the highest  $r$  square, were used in the trend analyses. In the present study, volume adjustment of precipitation chemistry was seldom necessary because correlations between precipitation chemistry and precipitation amount generally were poor. Unless otherwise noted, the stream water results being presented pertain to flow-adjusted concentrations, which are referred to simply as “concentrations” for brevity. Concentrations not adjusted for variations related to flow are referred to as “raw concentrations.”

The SKT allows for selection of the number of seasons to use in the trend analyses. Because the minimum sampling frequency at the HBN sites was quarterly, trends in stream water chemistry were tested using four seasons of equal duration. When more than one sample was collected in a given season, the sample nearest the midpoint of the season was used. For precipitation data, trend analyses were performed on quarterly volume-weighted mean values reported by the NADP [1984–96]. Trends with  $p$  values less than 0.01 were considered highly significant, those between 0.01 and 0.05 were considered moderately significant, and those between 0.05 and



**Figure 3.** Variations in SO<sub>4</sub>, Ca + Mg, alkalinity, and instantaneous discharge at the Wild River, Maine, and SO<sub>4</sub>, Ca + Mg, hydrogen, and precipitation amount at Bridgeton, Maine (circles), and Hubbard Brook, New Hampshire (crosses). Trend lines were generated by a locally weighted scatterplot smoothing technique (LOWESS). Results of seasonal Kendall trend tests shown on graphs pertain to the period October 1967 through September 1996 for stream water and from the time of station installation through September 1996 for precipitation. Results are presented as follows:  $s$ , slope of raw concentration trend;  $p$ ,  $p$  value of raw concentration trend;  $s_a$ , slope of flow- or volume-adjusted concentration trend;  $p_a$ ,  $p$  value of flow- or volume-adjusted concentration trend. Results for flow- or volume-adjusted concentration trends are shown only when adjustment model was significant at  $p < 0.1$ .

0.1 were considered weakly significant. A  $p$  value greater than 0.1 was interpreted to indicate no significant trend.

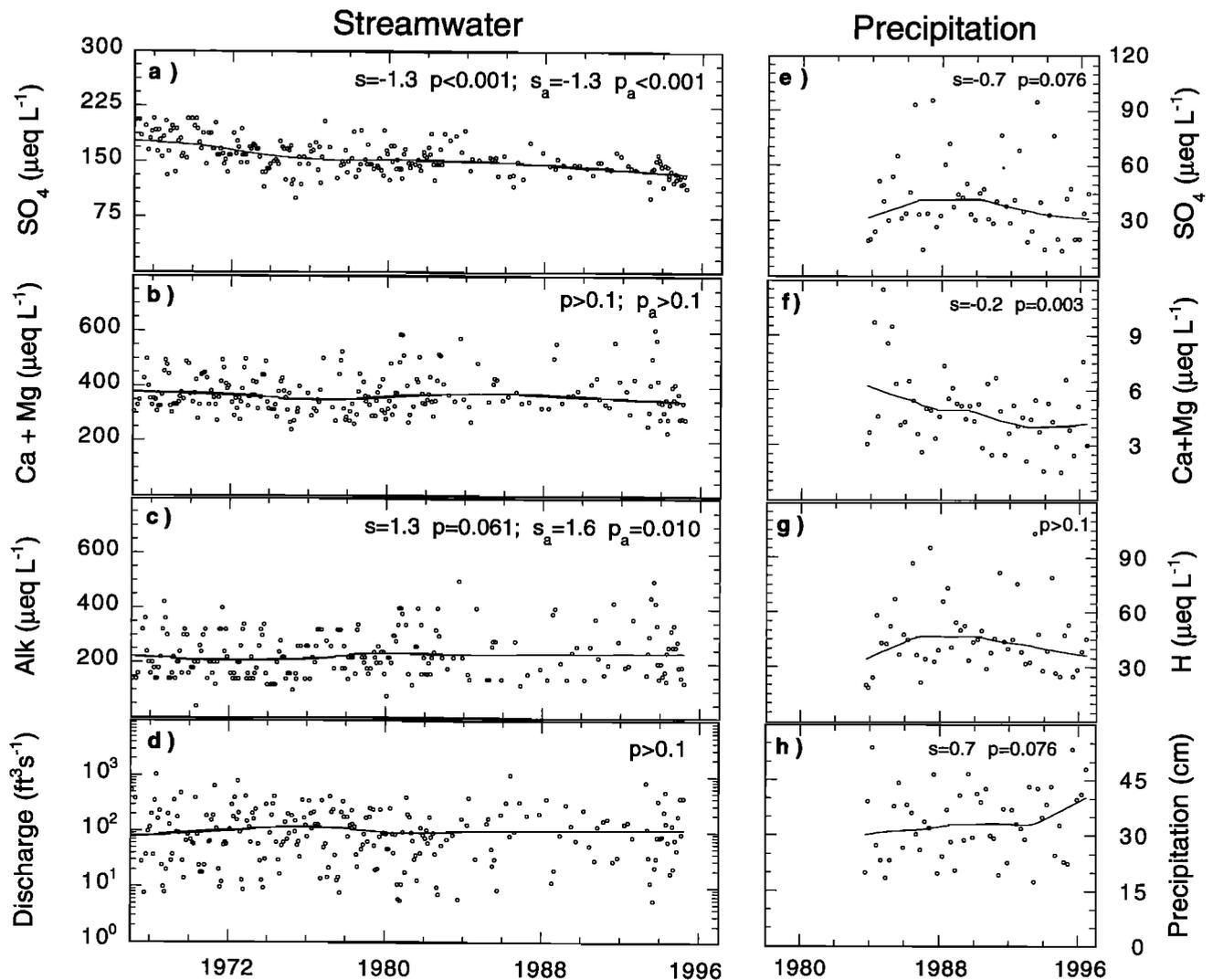
The direction and slope of trends were obtained using the Sen slope estimator, which calculates the median of the slopes of all pairwise comparisons [Helsel and Hirsch, 1992]. Stream water and precipitation concentrations were plotted against time with a smoothed, locally weighted regression line (LOWESS) as an overlay to show general patterns in the data. The LOWESS technique is a nonparametric smoothing procedure that uses a weighted, least squares regression model to fit observations within a specified window [Cleveland, 1979], which in this case was set to 0.5. It is a useful exploratory tool because it fits a regression model through data without making

any assumptions about what type of model the data might fit (linear, quadratic, etc.).

### 3. Results

#### 3.1. Trends in Stream Water Chemistry

Concentrations of SO<sub>4</sub> in stream water exhibited highly significant decreases between 1968 and 1996 at three of the five HBN study sites: Wild River (Maine), Esopus Creek (N. Y.), and Holiday Creek (Va.) (Figures 3a, 4a, 5a, 6a, and 7a). The slopes of the SO<sub>4</sub> trends at these sites ranged from  $-0.9$  to  $-1.3 \mu\text{eq L}^{-1} \text{yr}^{-1}$  (Figures 3a, 4a, 5a, 6a, and 7a). The downward trends in SO<sub>4</sub> at the Wild River and Esopus Creek were



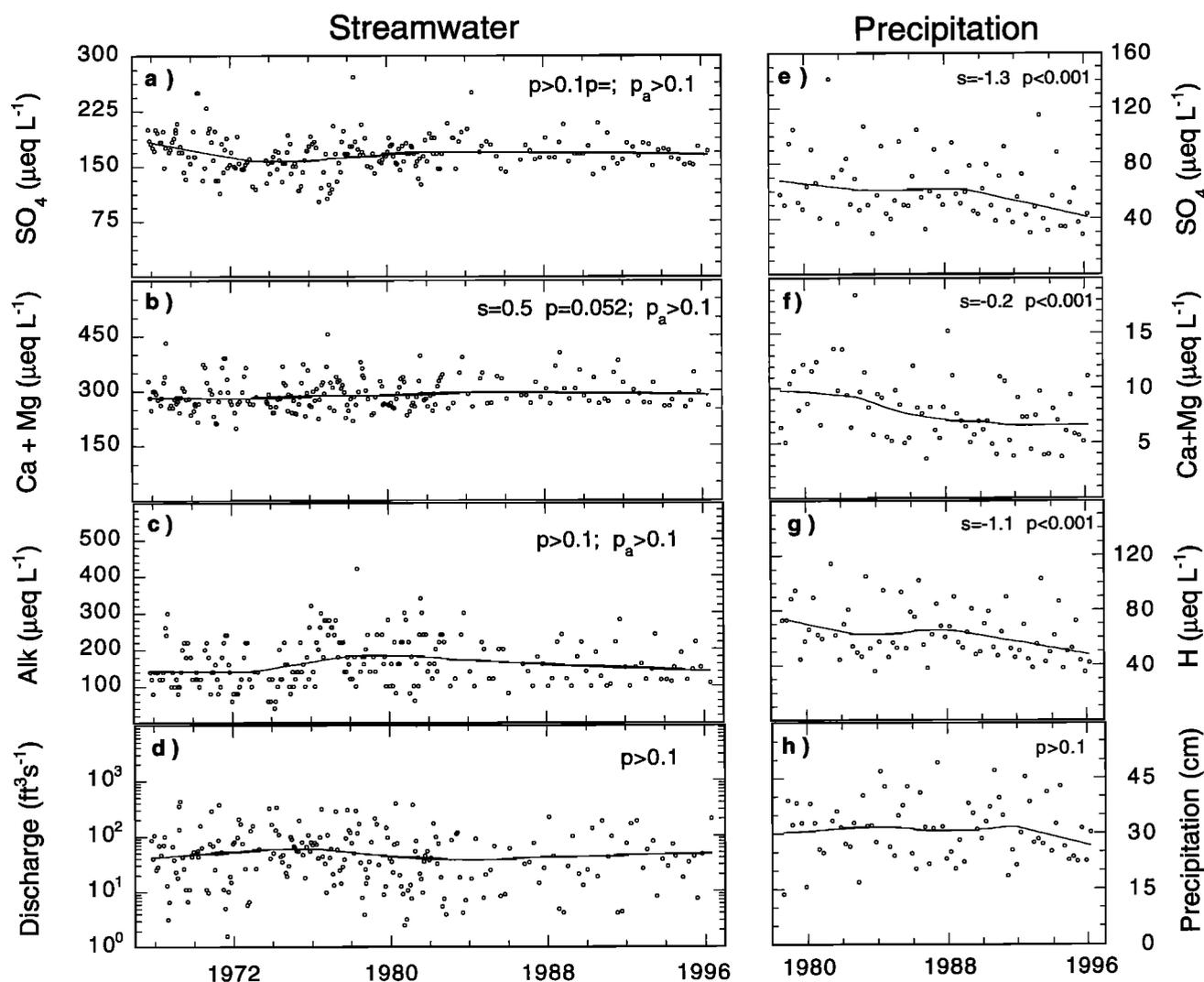
**Figure 4.** Variations in  $\text{SO}_4$ , Ca + Mg, alkalinity, and instantaneous discharge at Esopus Creek, New York, and  $\text{SO}_4$ , Ca + Mg, hydrogen, and precipitation amount at Biscuit Brook, New York. Periods covered and presentation of results are as indicated in Figure 3.

relatively steady; when the period of record was divided into 1968–1983 and 1984–1996, both sites had significant downward trends during each period (Table 2). Most of the long-term decline in  $\text{SO}_4$  at Holiday Creek was attributable to a strong decline that began in the late 1970s (Figure 6a, Table 2). Although no trends were detected over the long-term (1968–1996) at Young Womans Creek (Pa.) and Upper Twin Creek (Ohio), both sites did have significant downward trends in  $\text{SO}_4$  during the latter half of the record (1984–1996, Table 2). Upper Twin Creek had the only significant upward trend in  $\text{SO}_4$ , which was a strong increase during 1968–1983.

Despite the complexity of the trends in  $\text{SO}_4$  concentrations in the HBN streams, some generalizations can be made. From 1968 through 1983, trends in  $\text{SO}_4$  at the HBN sites were varied;  $\text{SO}_4$  at the northernmost sites decreased,  $\text{SO}_4$  at sites in Pennsylvania and Virginia showed no change, and  $\text{SO}_4$  at the site in Ohio increased. From 1984 through 1996,  $\text{SO}_4$  trends appear to have been somewhat more uniform. During 1984–1996,  $\text{SO}_4$  exhibited strong to moderate declines at all of the sites, with slopes ranging from  $-1.3$  to  $-5.1 \mu\text{eq L}^{-1} \text{yr}^{-1}$ .

The stream water  $\text{SO}_4$  trend results obtained for the 1968–1983 period are in good agreement with those reported by *Smith and Alexander* [1983] and *Kramer et al.* [1986] for HBN sites in the northeastern United States between the mid 1960s and early 1980s. *Kramer et al.* [1986] noted downward trends in  $\text{SO}_4$  at the Wild River and Esopus Creek during the period (slopes =  $-1.5$  and  $-1.8 \mu\text{eq L}^{-1} \text{yr}^{-1}$ , respectively), and no significant trends at Young Womans Creek or Holiday Creek. A downward trend in  $\text{SO}_4$  of  $2 \mu\text{eq L}^{-1} \text{yr}^{-1}$  has been reported for 1963–1993 at Hubbard Brook, in New Hampshire, 50 km west of the Wild River HBN site [*Driscoll et al.*, 1989; *Likens et al.*, 1996]. *Aulenbach et al.* [1996] reported a downward trend in  $\text{SO}_4$  between the early 1980s and early 1990s at Biscuit Brook, a small headwater stream 5 km southwest of Esopus Creek. Interestingly, they detected few significant trends in stream water  $\text{SO}_4$  in the southeastern United States, perhaps because soils in the southeast generally have high sulfate-adsorption capacities [*Aulenbach et al.*, 1996].

Long-term (1968–1996) trends in Ca + Mg included a highly significant downward trend at the Wild River, and a highly



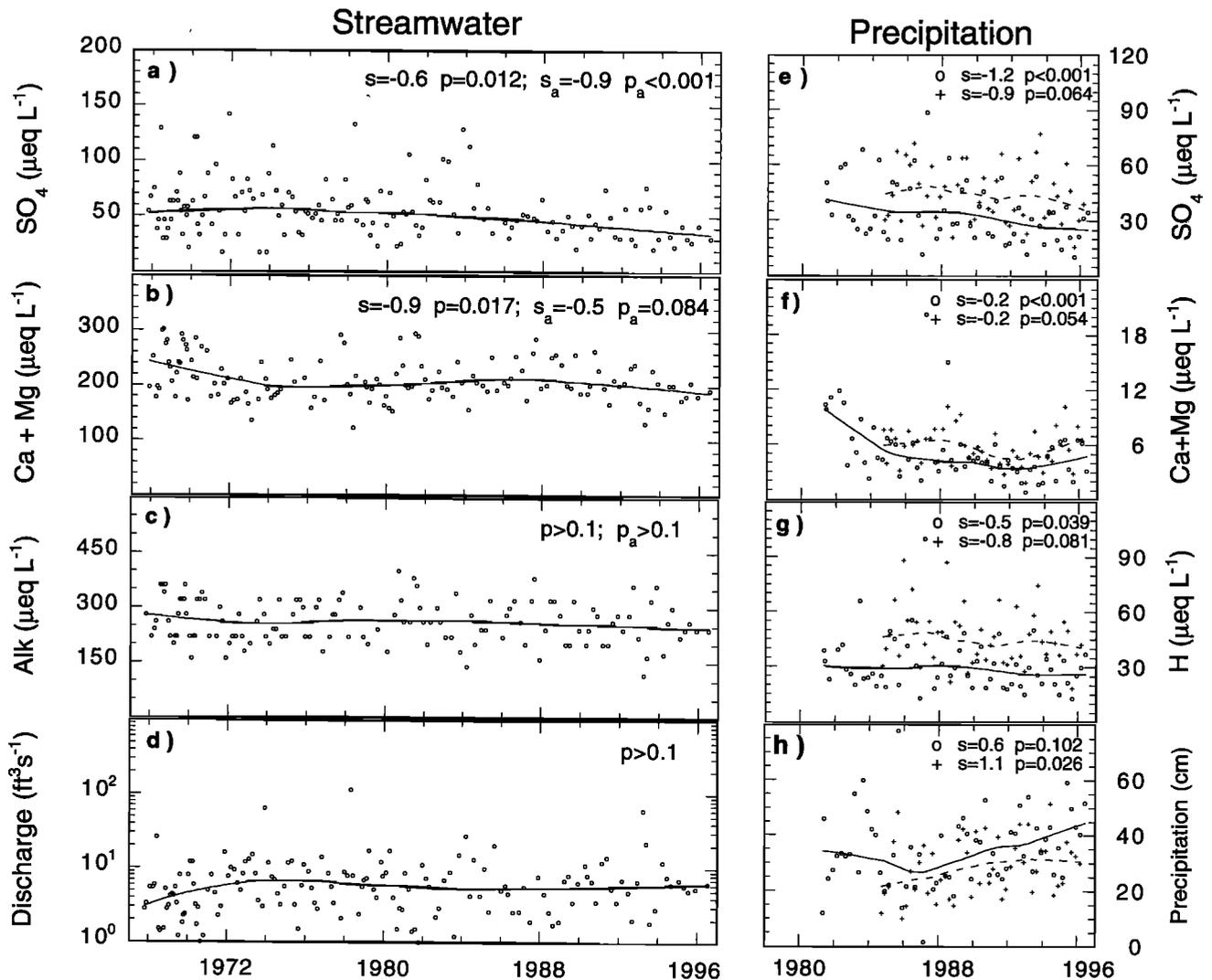
**Figure 5.** Variations in SO<sub>4</sub>, Ca + Mg, alkalinity, and instantaneous discharge at Young Womans Creek, Pennsylvania, and SO<sub>4</sub>, Ca + Mg, hydrogen, and precipitation amount at Kane Experimental Forest, Pennsylvania. Periods covered and presentation of results are as indicated in Figure 3.

significant upward trend at Upper Twin Creek (Figures 3b and 7b). The decline in Ca + Mg at the Wild River was persistent throughout the period of record (Figure 3b, Table 2). The long-term upward trend in Ca + Mg at Upper Twin Creek was mainly due to a strong increase during the first half of the record (Figure 7b, Table 2). In addition to the decline in Ca + Mg at the Wild River during 1984–1996, highly significant decreases also were detected at Esopus Creek and Holiday Creek for the same period (Table 2). The magnitude of the declines in Ca + Mg at the Wild River and Holiday Creek during 1984–1996 were similar to the declines in SO<sub>4</sub>, but at Esopus Creek, Ca + Mg decreased about twice as much as SO<sub>4</sub>. Although not statistically significant ( $p = 0.186$ ), a decrease in Cl of sufficient magnitude to account for the difference in SO<sub>4</sub> and Ca + Mg trends at Esopus Creek is suggested by the slope of the Cl “trend” ( $-3.8 \mu\text{eq L}^{-1} \text{yr}^{-1}$ ). Decreasing Cl might be attributable to declining use of and contamination from road deicing salts, which often also contain Mg.

Long-term (1968–1996) trends in alkalinity included a moderately significant downward trend at the Wild River and a

highly significant upward trend at Upper Twin Creek (Figures 3c and 7c). Most of the increase in alkalinity at Upper Twin Creek occurred during the 1984–1996 period, a time that coincided with a decrease in SO<sub>4</sub> and stable Ca + Mg concentrations (Table 2, Figure 7). The long-term decline in alkalinity at the Wild River is somewhat puzzling because when the data set was broken into 1968–1983 and 1984–1996, trends in alkalinity were not significant during either period at  $p < 0.1$ . Although there were no reported methods changes, the scarcity of high alkalinity values during the second half of the record is suggestive of a step function, so interpretation of long-term trends in alkalinity at the Wild River must be done with caution. The only other significant trend in alkalinity was a weak upward trend at Esopus Creek during 1968–1983 (Table 2).

Trends in alkalinity generally reflected a balance between trends in SO<sub>4</sub> and Ca + Mg. When SO<sub>4</sub> decreased and Ca + Mg concentrations were stable, alkalinity tended to show an increase. Specific examples include Upper Twin Creek from 1984 through 1996 and Esopus Creek during 1968–1983. Conversely, when trends in SO<sub>4</sub> were roughly matched by trends in



**Figure 6.** Variations in SO<sub>4</sub>, Ca + Mg, alkalinity, and instantaneous discharge at Holiday Creek, Virginia, and SO<sub>4</sub>, Ca + Mg, hydrogen, and precipitation amount at Shenandoah, Virginia (circles), and Charlottesville, Virginia (crosses). Periods covered and presentation of results are as indicated in Figure 3.

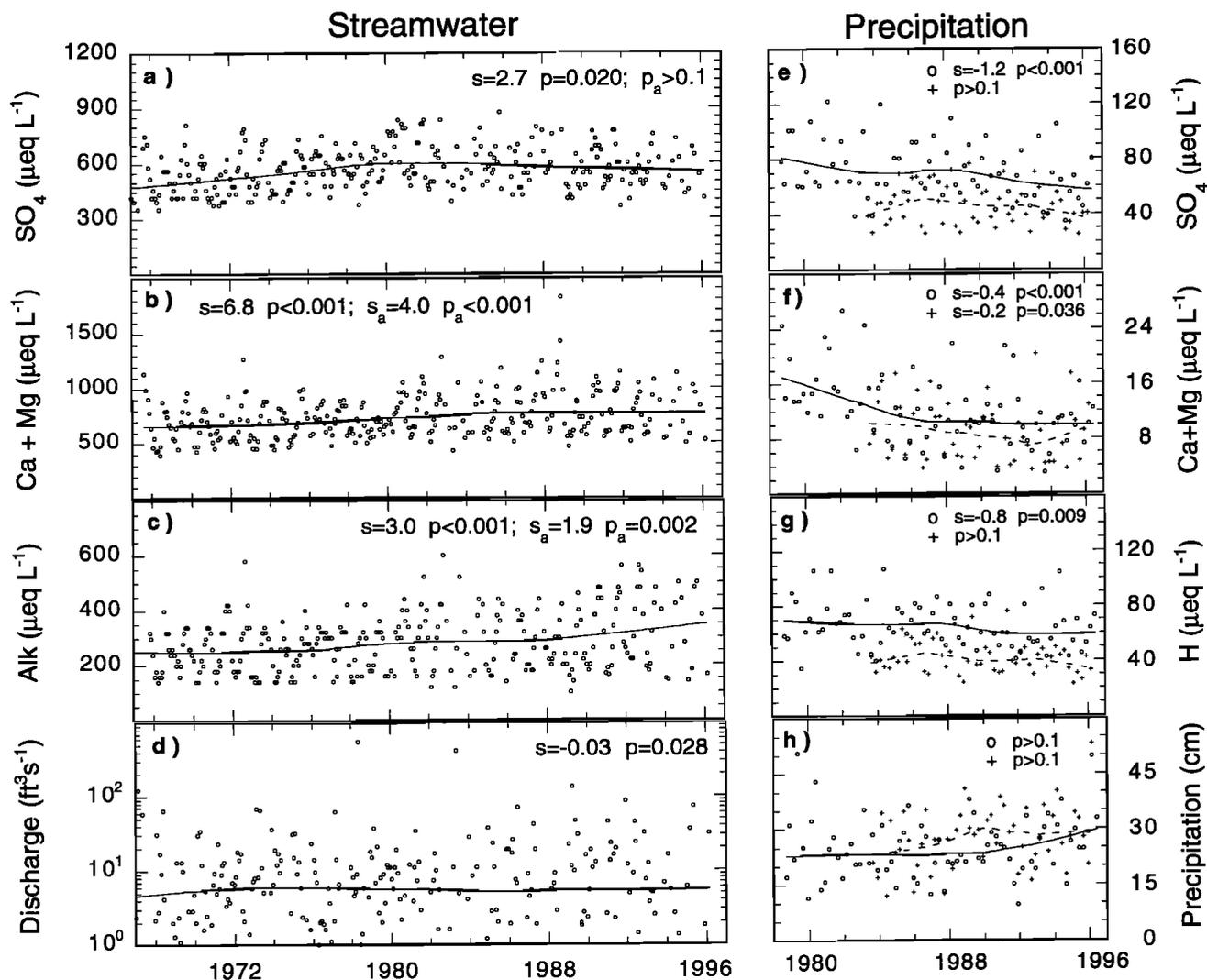
Ca + Mg, changes in alkalinity generally were not significant. This was the case at Upper Twin Creek between 1968 and 1983, where the SO<sub>4</sub> and Ca + Mg increased, and the Wild River and Holiday Creek during 1984–1996, where SO<sub>4</sub> and Ca + Mg decreased. A regression of the slopes of the SO<sub>4</sub> trend minus the (Ca + Mg) trend against the alkalinity trend yielded a regression equation with a slope of  $-1.04$ , an  $r^2$  of  $0.85$ , and a  $p$  value of  $<0.001$ . This strong inverse relation is to be expected given charge balance constraints and the fact that SO<sub>4</sub>, Ca, Mg, and alkalinity generally were the dominant ions in stream water.

Trends in raw concentrations and flow-adjusted concentrations generally were similar, which is reasonable because there were few significant trends in discharge (Table 2; Figures 3d, 4d, 5d, 6d, and 7d). The only two trends in discharge were moderately significant declines that occurred at Upper Twin Creek during 1968–1983 (also reflected in the long-term trend) and at Esopus Creek during 1984–1996 (Table 2). Declining discharge at Upper Twin Creek was partly responsible for the increase in raw concentrations of SO<sub>4</sub>, Ca + Mg, and alkalinity

observed during the 1968–1983 period (Table 2). Although trends in raw concentrations and flow-adjusted concentrations of SO<sub>4</sub>, Ca + Mg, and alkalinity were all upward at Upper Twin Creek during 1968–1983, trend tests on raw concentrations gave larger trend slopes and smaller  $p$  values than tests on flow-adjusted concentrations. At Esopus Creek the downward trend in discharge between 1984 and 1996 led to a similar situation; trend tests on raw alkalinity indicated a significant upward trend, but tests on flow-adjusted concentrations did not. In addition, the downward trend in discharge at Esopus Creek masked a decline in base cation concentrations that appeared only in the flow-adjusted data.

### 3.2. Trends in Precipitation Chemistry

Five of the eight NADP sites had highly significant declines in SO<sub>4</sub> between 1984 and 1996, two had weakly significant declines, and one exhibited no significant trend (Table 3). At the sites with significant trends, decreases ranged from  $0.70$  to  $1.99 \mu\text{eq L}^{-1} \text{yr}^{-1}$ . The LOWESS curves in Figures 3e, 4e, 5e, 6e, and 7e suggest that SO<sub>4</sub> concentrations generally declined



**Figure 7.** Variations in SO<sub>4</sub>, Ca + Mg, alkalinity, and instantaneous discharge at Upper Twin Creek, Ohio, and SO<sub>4</sub>, Ca + Mg, hydrogen, and precipitation amount at Caldwell, Ohio (circles), and Clark State Fish Hatchery, Kentucky (crosses). Periods covered and presentation of results are as indicated in Figure 3.

between the late 1970s and about 1984, then leveled off until about 1988, and then resumed declining.

Concentrations of Ca + Mg in precipitation exhibited highly significant declines at two of eight NADP sites between 1984 and 1996, and moderate or weak declines occurred at five sites (Table 3). Although the downward trends were pervasive, the magnitudes of decline were much less than for SO<sub>4</sub>, ranging from 0.11 to 0.26 μeq L<sup>-1</sup> yr<sup>-1</sup>. The LOWESS curves indicate that most of the declines in Ca + Mg occurred during the 1980s, and concentrations during the 1990s generally appeared stable (Figures 3f, 4f, 5f, 6f, and 7f).

Concentrations of H in precipitation decreased at five of the eight sites between 1984 and 1996 (Table 3). Where significant, the temporal patterns of the H declines were similar to those of SO<sub>4</sub>. The LOWESS curves suggest declines during the late 1970s to early 1980s, then a stable period until about 1988, followed by another period of decline (Figures 3g, 4g, 5g, 6g, and 7g).

In the preceding discussion the precipitation trend results focused on the 1984–1996 period in order to provide a consistent period with which stream water trends could be compared.

However, it is interesting to consider the trend results obtained when the entire precipitation data record for each site is analyzed. The slopes and *p* values of these results are presented in the upper right of Figures 3–7. It should be noted that because the NADP stations had varying start-up times, intercomparison of results among sites using the entire record for each site is problematic. At the five sites with startup dates prior to 1984, trend analyses on data covering the entire period of record for each site yielded lower *p* values in nearly every case than when trends were run on the 1984–1996 data subset. Concentrations of SO<sub>4</sub>, Ca + Mg, and H decreased at each of the five sites, and in 13 out of 15 cases, *p* values were highly significant. These results add supporting evidence for consistent downward trends in SO<sub>4</sub>, Ca + Mg, and H in precipitation in the northeastern United States from the early 1980s through the mid 1990s.

The trends in precipitation SO<sub>4</sub> observed in this study generally are similar to those reported by other investigators for NADP sites in the northeastern United States for the early 1980s to early 1990s [Hedin *et al.*, 1994; Lynch *et al.*, 1995a, b]. In contrast with those studies, however, is the similarity found

**Table 2.** Results of Seasonal Kendall Trend Tests on Stream Water Data Using Raw Concentrations and Flow-Adjusted Concentrations

	Discharge, fcet <sup>3</sup> s <sup>-1</sup> yr <sup>-1</sup>	SO <sub>4</sub> , $\mu\text{eq}$ L <sup>-1</sup> yr <sup>-1</sup>	Ca + Mg, $\mu\text{eq L}^{-1}$ yr <sup>-1</sup>	Alkalinity, $\mu\text{eq L}^{-1}$ yr <sup>-1</sup>
<i>Water Years 1968–1983</i>				
Wild River, Maine				
Trend	0.25 (0.835)	-1.3 (0.031)	-1.2 (0.027)	0.0 (0.675)
Flow-adjusted trend	...	n.s.	-0.8 (0.030)	0.1 (0.887)
Esopus Creek, N. Y.				
Trend	-2.00 (0.167)	-1.6 (0.011)	0.3 (0.759)	4.0 (0.016)
Flow-adjusted trend	...	-1.5 (0.009)	-0.8 (0.410)	3.1 (0.088)
Young Womans Creek, Pa.				
Trend	0.00 (0.927)	-0.6 (0.368)	0.0 (0.869)	1.4 (0.172)
Flow-adjusted trend	...	-0.7 (0.407)	-0.3 (0.511)	1.2 (0.290)
Holiday Creek, Va.				
Trend	0.00 (1.000)	0.3 (0.427)	-1.3 (0.119)	0.0 (0.976)
Flow-adjusted trend	...	0.6 (0.246)	-1.4 (0.126)	-0.6 (0.477)
Upper Twin Creek, Ohio				
Trend	-0.14 (0.036)	8.5 (0.000)	13.1 (0.000)	3.2 (0.024)
Flow-adjusted trend	...	6.5 (0.001)	7.5 (0.003)	2.4 (0.131)
<i>Water Years 1984–1996</i>				
Wild River, Maine				
Trend	-1.75 (0.432)	-1.3 (0.002)	-1.2 (0.002)	0.0 (0.367)
Flow-adjusted trend	...	-1.3 (0.001)	-1.4 (0.003)	-0.9 (0.167)
Esopus Creek, N. Y.				
Trend	-6.22 (0.038)	-1.6 (0.035)	-0.2 (0.855)	7.6 (0.020)
Flow-adjusted trend	...	-2.2 (0.005)	-5.4 (0.008)	2.4 (0.243)
Young Womans Creek, Pa.				
Trend	1.37 (0.124)	-1.2 (0.107)	-1.3 (0.127)	0.0 (0.617)
Flow-adjusted trend	...	-1.4 (0.036)	-0.6 (0.148)	1.1 (0.124)
Holiday Creek, Va.				
Trend	0.09 (0.540)	-1.6 (0.027)	-3.6 (0.007)	0.0 (0.331)
Flow-adjusted trend	...	-2.5 (0.000)	-3.1 (0.000)	0.0 (0.926)
Upper Twin Creek, Ohio				
Trend	0.04 (0.439)	-6.9 (0.047)	-3.2 (0.519)	4.0 (0.025)
Flow-adjusted trend	...	-5.1 (0.048)	1.5 (0.629)	6.1 (0.000)

The *p* values of trends are given in parentheses; n.s., flow adjustment model was not significant. One cubic foot equals 0.028 m<sup>3</sup>.

in the present study among trends in SO<sub>4</sub> and H (Table 3). *Hedin et al.* [1994] and *Lynch et al.* [1995a] reported that between 1980 and 1990–1993, declines in base cations tended to offset decreases in SO<sub>4</sub>, and as a result, significant changes in precipitation acidity were seldom observed. The present analysis indicates that in most cases, declines in SO<sub>4</sub> were nearly matched by decreases in H. The differences in results may be due to any of several factors, including (1) the possibility of greater variance in H than in SO<sub>4</sub> and Ca + Mg, making trend detection relatively difficult; (2) analysis of data from different time periods; or (3) use of different statistical techniques (parametric versus nonparametric). Precipitation acidity may be affected by a variety of solutes including SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub>, organic acids, and base cations. Thus variations in compounds other than SO<sub>4</sub> and base cations contribute to the variability in H: high variability reduces the power of statistical tests to detect trends. The issue of differences in the time period analyzed is important because of recent changes in the ratio of SO<sub>4</sub>:(Ca + Mg) in precipitation. In the mid 1990s, although SO<sub>4</sub> continued a decline that began in the late 1980s, Ca + Mg stabilized (see Figures 3e, 4e, 5e, 6e, and Figures 3f, 4f, 5f, 6f, and 7f). The greater preponderance of downward trends in H in the present study may reflect a lower SO<sub>4</sub>:(Ca + Mg) ratio in precipitation in the mid 1990s. Data from the mid 1990s were not available to *Hedin et al.* [1994] or *Lynch et al.* [1995a] when they did their studies. However, *Lynch and Bowersox* [1996] did analyze data through 1995, and they noted a

decline in precipitation acidity in 1995 in the northeastern United States. They also reported that declines in SO<sub>4</sub> and H were highly correlated ( $r^2 = 0.72$ ).

## 4. Discussion

### 4.1. Evaluation of Possible Causes of Stream Water Trends

The results of the trend analyses indicate that SO<sub>4</sub> concentrations declined between 1984 and 1996 at all of the stream water sites and nearly all of the precipitation sites examined in this study. In the following discussion we investigate possible causes for the trends in stream water chemistry, including potential linkages with trends in atmospheric deposition, changes in analytical methodology, and changes in land use in the study basins.

The similarity in extent and direction of the stream water and precipitation trends suggests that the declines in stream water SO<sub>4</sub> might be related to the downward trends in SO<sub>4</sub> deposition. For changes in atmospheric deposition to be the main cause of changes in stream water SO<sub>4</sub>, two conditions were considered necessary. First, in order for changes in atmospheric deposition to result in major changes in stream water SO<sub>4</sub> concentrations, atmospheric deposition would have to account for a substantial portion of total sulfur inputs to the basins. Second, assuming other outside perturbations are minimal, changes in atmospheric deposition and stream water SO<sub>4</sub> would need to be similar in magnitude. These conditions were

**Table 3.** Results of Seasonal Kendall Trend Tests on Precipitation Data Using Raw Concentrations and Volume-Adjusted Concentrations, Water Years 1984–1996

	Precipitation, cm yr <sup>-1</sup>	SO <sub>4</sub> , μeq L <sup>-1</sup> yr <sup>-1</sup>	Ca + Mg, μeq L <sup>-1</sup> yr <sup>-1</sup>	Hydrogen, μeq L <sup>-1</sup> yr <sup>-1</sup>
Bridgeton, Maine (ME02)				
Trend	0.16 (0.723)	-0.85 (0.002)	-0.17 (0.031)	-0.69 (0.124)
Volume-adjusted trend	...	n.s.	n.s.	n.s.
Hubbard Brook, N. H. (NH02)				
Trend	0.02 (0.877)	-0.95 (0.000)	-0.26 (0.000)	-0.43 (0.013)
Volume-adjusted trend	...	n.s.	n.s.	n.s.
Biscuit Brook, N. Y. (NY68)				
Trend	0.66 (0.076)	-0.70 (0.076)	-0.19 (0.003)	-0.79 (0.288)
Volume-adjusted trend	...	n.s.	n.s.	-0.48 (0.166)
Kane Experimental Forest, Pa. (PA29)				
Trend	-0.26 (0.135)	-1.30 (0.001)	-0.14 (0.063)	-1.27 (0.003)
Volume-adjusted trend	...	-1.15 (0.007)	n.s.	n.s.
Charlottesville, Va. (VA00)				
Trend	1.05 (0.026)	-0.85 (0.064)	-0.19 (0.054)	-0.84 (0.081)
Volume-adjusted trend	...	n.s.	n.s.	n.s.
Shenandoah, Va. (VA28)				
Trend	1.18 (0.023)	-1.33 (0.000)	-0.11 (0.038)	-0.73 (0.053)
Volume-adjusted trend	...	n.s.	n.s.	n.s.
Caldwell, Ohio (OH49)				
Trend	0.63 (0.049)	-1.39 (0.006)	-0.15 (0.186)	-1.17 (0.057)
Volume-adjusted trend	...	-1.99 (0.001)	n.s.	-1.45 (0.011)
Clark State Fish Hatchery, Ky. (KY35)				
Trend	0.56 (0.130)	-0.25 (0.499)	-0.23 (0.036)	-0.45 (0.333)
Volume-adjusted trend	...	n.s.	n.s.	n.s.

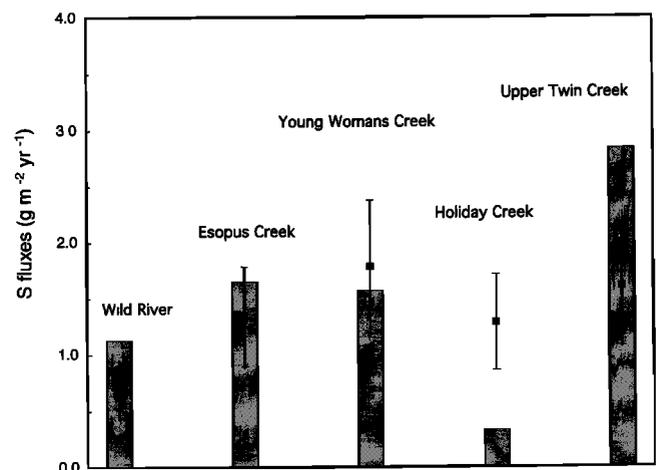
The *p* values of trends are given in parentheses; n.s., volume adjustment model was not significant.

evaluated by comparing fluxes of sulfur into and out of the basins and by comparing the slopes of trends in SO<sub>4</sub> concentrations in atmospheric deposition and stream water.

Only a qualitative assessment of stream water sulfur fluxes is possible at the HBN study sites because of the low frequency of sampling; however, a general comparison is possible. Average annual stream water fluxes of SO<sub>4</sub> were estimated for 1984–1995 by calculating a discharge-weighted mean concentration for each year and multiplying by the annual discharge, then averaging the results. Average annual fluxes of SO<sub>4</sub> from the atmosphere for the 1984–1995 period were calculated as the sum of wet deposition plus dry deposition. Wet deposition values were obtained from the NADP, which calculates deposition by multiplying precipitation concentrations times volume in weekly samples [NADP, 1984–1996]. Dry deposition is highly variable and difficult to quantify, but estimates typically range from 25% to 100% of wet deposition [Lindberg *et al.*, 1986; Meyers and Sisterson, 1991; Lovett *et al.*, 1997]. Total atmospheric deposition of SO<sub>4</sub> was estimated using assumptions of dry deposition being equal to 0, 0.5, and 1 times wet deposition. Results indicate that at Esopus Creek, Young Womans Creek, and Holiday Creek, atmospheric deposition can account for the majority of SO<sub>4</sub> exported via stream water (Figure 8). At Holiday Creek, atmospheric inputs greatly exceed stream exports of SO<sub>4</sub>, probably because of SO<sub>4</sub> adsorption in the clay-rich soils. At the Wild River and Upper Twin Creek, SO<sub>4</sub> export exceeds estimated atmospheric SO<sub>4</sub> inputs by 10% to 60%, indicating that there probably is an internal source of SO<sub>4</sub> in those basins, such as weathering of sulfide minerals. Despite the apparent mineralogic source of sulfur in the Wild River and Upper Twin Creek basins, atmospheric deposition appears to contribute the majority of SO<sub>4</sub> to streams at those sites as well as at the other HBN streams in the northeast.

Slopes of trends in SO<sub>4</sub> in atmospheric deposition and stream water between 1984 and 1996 were compared after

accounting for dry deposition and evapotranspiration. For simplicity it was assumed that relative changes in dry deposition were equal to relative changes in wet deposition. Under that assumption, changes in total atmospheric deposition would be greater than for wet deposition alone. The effect of evapotranspiration on stream water was accounted for by multiplying the stream water trend slope by the estimated water yield for each basin [Mast and Turk, 1998]. In four of five cases, declines in atmospheric deposition were more than sufficient to account for virtually all of the decline in stream water SO<sub>4</sub>, even under the assumption of zero dry deposition (Table 4).



**Figure 8.** Estimated fluxes of S in stream water and atmospheric deposition for 1984–1995. Columns indicate stream water fluxes. Square symbols and attached error bars indicate estimated S fluxes in atmospheric deposition under assumptions of zero dry deposition (lower error bar), dry deposition = 0.5 times wet deposition (square), and dry deposition = 1.0 times wet deposition (upper error bar).

**Table 4.** Estimated Percentage of Change in SO<sub>4</sub> and Ca + Mg in Stream Water Attributable to Change in SO<sub>4</sub> and Ca + Mg in Atmospheric Deposition During 1984–1996

	Wet Deposition Trend Slope	Adjusted Stream Water Trend Slope	Atmospheric Deposition Slope/Stream Water Slope		
			dd = 0, %	dd = 0.5 × wet, %	dd = 1 × wet, %
<i>SO<sub>4</sub></i>					
Wild River	-0.90	-0.95	95	142	190
Esopus Creek	-0.70	-1.35	52	78	104
Young Womans Creek	-1.15	-0.73	158	236	316
Holiday Creek	-1.09	-0.87	125	188	250
Upper Twin Creek	-1.99	-1.85	108	162	216
<i>Ca + Mg</i>					
Wild River	-0.21	-1.03	20	31	41
Esopus Creek	-0.19	-3.32	6	9	11
Young Womans Creek	-0.14	n.s.	...	...	...
Holiday Creek	-0.15	-1.08	14	21	28
Upper Twin Creek	n.s.	n.s.	...	...	...

The stream water trends were adjusted for evapotranspiration. Three dry-deposition (dd) scenarios are provided, including zero dry deposition, dry deposition = 0.5 × wet deposition, and dry deposition = 1.0 × wet deposition. Here n.s., trend was not significant.

Slopes of trends in Ca + Mg also were compared in order to evaluate whether changes in stream water concentrations might be attributable to changes in atmospheric deposition. Results indicate that declines in atmospheric deposition can account for between 6% and 41% of the decreases in stream water Ca + Mg between 1984–1996 (Table 4). These percentages are substantially less than values reported for Hubbard Brook [Driscoll *et al.*, 1989; Likens *et al.*, 1996], where declines in atmospheric deposition of base cations were estimated to account for between 77% and 85% of the declines in stream water base cations since the mid 1960s [Driscoll *et al.*, 1989; Likens *et al.*, 1996]. Most of the decline in base-cation deposition at Hubbard Brook occurred prior to the mid-1970s, so the difference in results probably is due to use of a longer record in the Hubbard Brook analysis.

The decline in stream water base-cation concentrations at Hubbard Brook and at the HBN streams may be due to reduced leaching of cations from the soil-exchange pool. According to the mobile acid anion theory, hydrogen associated with strong acid anions deposited from the atmosphere displaces cations on soil exchange sites, which then leach from the soil with mobile anions such as SO<sub>4</sub> [Galloway *et al.*, 1983]. However, as acidic deposition declines, fewer mobile acid anions are flushed through the soil and leaching of cations from the exchange pool decreases. It is important to note that although acidic deposition rates and cation leaching may be declining, cations will continue to be depleted from the exchange pool as long as the leaching rate is greater than the rate of cation resupply from mineral weathering and atmospheric deposition (assuming no net uptake or release by vegetation). This may be manifested in stream water chemistry as a decline in SO<sub>4</sub> and base cation concentrations and relatively invariant pH and alkalinity, a pattern which is evident at Hubbard Brook and some of the HBN streams.

The second possible explanation for the declines in stream water SO<sub>4</sub> noted in this study that was explored was changes in analytical methods. As described in the methods section, the bias on blind-audit samples analyzed by the USGS central laboratory was tested for trends and inspected for step functions. Two periods of bias in SO<sub>4</sub> results were identified, and the concentrations of blind-audit and natural samples were adjusted as previously noted. Prior to adjustment, the bias in the results for the blind-audit samples exhibited a downward trend from 1984–1996 ( $p < 0.001$ ), but after adjustment no

trend in bias was apparent ( $p > 0.5$ ). The effect of the bias during January 1995 to mid 1996 was more pronounced than the bias in the late 1980s because the former occurred near the end of the record rather than in the middle of the record. Trend tests on the stream water 1984–1996 SO<sub>4</sub> data sets prior to and after adjustment indicated downward trends in adjusted and unadjusted data at all sites, but the trends in the unadjusted data were generally stronger and had slopes of greater magnitude than trends in the adjusted data. Exclusion of the suspect data from the analyses usually did not substantially change the results of the statistical tests, although in some cases  $p$  values of trend tests were higher than they would have been otherwise, probably because gaps in the data records reduced the power of the statistical tests. As an additional test for bias in analytical results, SO<sub>4</sub> concentrations in water samples collected at Crater Lake, Oregon (a USGS HBN site) and analyzed at the USGS central laboratory were tested for trends. Because the residence time of water in Crater Lake is in excess of 100 years and the water is well mixed, concentrations should be relatively invariant on the time scale of this study. In effect, the Crater Lake water can serve as a large volume of natural reference water. No significant trends were identified in the adjusted Crater Lake SO<sub>4</sub> data for the periods 1968–1983 or 1984–1996, but a very weak downward trend during 1984–1996 was detected in the unadjusted data ( $p = 0.1$ ). Although it is always difficult to prove a complete lack of analytically driven trends, the results of the trend analyses on the blind-audit samples, the Crater Lake samples, and the various forms of the stream water data set suggest that analytical changes were not the main cause of trends identified in the HBN stream waters.

Land-use changes can affect surface-water quality in a variety of ways, and they were investigated as a third possible explanation for the downward trends in stream water SO<sub>4</sub>. Logging for example, might cause a short-term increase in NO<sub>3</sub> and base cation concentrations in streams and lakes because of decay of organic material [Hornbeck *et al.*, 1986; Binkley and Brown, 1993]. Conversely, reforestation removes base cations and NO<sub>3</sub> from solution via plant uptake and in the process releases acids. Construction activities disturb soils and expose fresh mineral surfaces, which can promote weathering. This may be manifested as an increase in alkalinity, silica, base cations, and potentially SO<sub>4</sub> concentrations in surface waters. Other types of land use that might impact surface-water quality include discharges from wastewater-treatment plants, which

can cause increased levels of Na, Cl, and nutrients in surface waters, and application of road deicing salts, which can release Na, Mg, and Cl to solution.

Changes in land use at the HBN basins in the northeast have been well documented by *Mast and Turk* [1998]. Logging occurred in most of the basins in the late 1800s and early 1900s, but most of the forests have recovered and are approaching maturity. Little logging has occurred recently in the Wild River, Esopus Creek, and Upper Twin Creek basins. Logging in the other basins involves selective cutting on a sustained yield basis with buffer strips between the cuts and surface water; less than 2% of the basin areas have been cut since the 1950s [*Mast and Turk*, 1998]. Thus it seems unlikely that timber harvesting would have much of an effect on stream water chemistry in any of the HBN basins. Similarly, because most forest stands are mature changes in biomass related to reforestation should be minimal, as was shown at Hubbard Brook [*Likens et al.*, 1996].

A few potentially important landscape disturbances have been documented in some of the HBN basins. In the early 1990s several wind storms and a pine-beetle infestation occurred in the Holiday Creek basin [*Mast and Turk*, 1998]. Although release of base cations and nutrients might be expected as dead timber decays, no increases in Ca + Mg or SO<sub>4</sub> concentrations in stream water were observed (Figures 3b, 4b, 5b, 6b, and 7b). Increased land disturbance is one plausible, albeit undocumented, explanation for the increases in SO<sub>4</sub> and Ca + Mg at Upper Twin Creek between 1968 and 1983. Exposure of bedrock during construction could increase weathering of pyrite from the shale, providing a source of SO<sub>4</sub>. The acidity released would tend to be neutralized by cation-exchange reactions, thus providing a source of Ca and Mg. Another plausible explanation for the increase in SO<sub>4</sub> and Ca + Mg between 1968 and 1983 at Upper Twin Creek is increasing acidic deposition. Increased acidic deposition would provide a direct source of SO<sub>4</sub> and would leach Ca and Mg from the soils. Although regional emissions of SO<sub>4</sub> have declined since 1970 [*Husar et al.*, 1991], local emissions sources might have had a different trend. A third possible source of Ca and Mg at Upper Twin Creek is dissolution of crushed limestone material that is used to surface gravel roads in the area; however, annual usage of crushed limestone has not been documented. Crushed limestone also is used on some of the gravel roads in the other HBN basins, but the mostly downward trends in Ca + Mg are not consistent with its having a large impact on stream water chemistry. Salts are used to deice roads in the winter in the Esopus Creek basin and appear to have a substantial effect on Na and Cl concentrations in stream water. Na and Cl increased by about 1.5  $\mu\text{eq L}^{-1} \text{yr}^{-1}$  between 1968 and 1983 ( $p < 0.1$ ), which coincides with a period of increasing population in the basin [*Mast and Turk*, 1998].

To summarize, changes in land use do not appear to have had a large effect on SO<sub>4</sub>, alkalinity, or Ca + Mg concentrations in the HBN streams in the northeast. One possible exception is at Upper Twin Creek from 1968 to 1983, where impacts from construction or road maintenance cannot be ruled out with the information currently available.

#### 4.2. Implications for Long-Term Monitoring Programs

Several implications pertaining to the design of long-term monitoring programs may be derived from this study. First, having a carefully designed quality-assurance program is essential. The use of blind-audit samples by the USGS central laboratory permitted identification of analytically driven trends

in SO<sub>4</sub> that could have otherwise confounded the interpretations. This illustrates the importance of routine analyses of blind samples that have a matrix similar to that of the natural waters being monitored. Other quality-assurance measures, including submittal of field blanks, analysis of spiked samples, and documentation of changes in sampling or analytical procedures are also important [*Ludtke and Woodworth*, 1997].

It is noteworthy that despite the relative infrequency of sample collection at the HBN streams, trends in concentrations were detected. Selection of a cost-effective sampling strategy is a major concern for managers of long-term monitoring networks. Although greater sampling frequency might improve the ability to detect trends, it costs more. One important benefit of increased sampling frequency is the ability to detect short-term trends with greater confidence. Basin size is another consideration when building a network designed to detect trends in stream water. It might be hypothesized that smaller basins, such as those used in many process-oriented studies, might be more responsive to changes in atmospheric deposition. However, it appears that the size of HBN basins is suitable for detection of trends attributable to changes in atmospheric deposition.

A design factor that might be more important than either sampling frequency or basin size is the continuity of the record. Sampling at some national surface-water monitoring networks, including the HBN and the U.S. Environmental Protection Agency's Long-Term Monitoring network, has been discontinued or drastically curtailed because of budget constraints. This has occurred just at the time when data records are of sufficient length to permit detection of long-term trends and when the effects of the Clean Air Act amendments of 1990 might be felt. Without continued monitoring, it will be difficult to assess the response of aquatic ecosystems to the mandated emissions reductions.

## 5. Conclusions

Downward trends in SO<sub>4</sub> concentrations occurred between 1984 and 1996 at each of five Hydrologic Benchmark Network streams in the northeastern United States and at seven of eight nearby precipitation monitoring stations. The consistency and similarity in direction and magnitude of stream water and precipitation trends in SO<sub>4</sub> suggest that streams may be exhibiting a regional response to changing atmospheric deposition. This decrease in stream water SO<sub>4</sub> is consistent with predictions made by conceptual ecosystem acidification models and with trends observed at intensively studied sites in the northeast, such as the Hubbard Brook Experimental Forest, New Hampshire.

Stream water alkalinity has not increased measurably at most of the HBN study sites in the northeast, despite widespread decreases in precipitation acidity. Similar temporal patterns of stream water alkalinity and precipitation acidity have been documented at Hubbard Brook, where reduced leaching of base cations from the soil exchange complex was implicated. Reduced base cation leaching could be caused by depletion of cations from the soil exchange complex or by declining rates of atmospheric deposition, and is supported as a regional phenomenon by strong declines in base cation concentrations in three of the HBN streams.

Although reductions in SO<sub>2</sub> emissions are now apparently being reflected in reduced precipitation and stream water sulfate concentrations, the reductions have not yet led to widespread increases in stream water alkalinity. Increases in alkalinity will be minimal until the rate of acidic deposition is reduced to substantially less than the rate of cation resupply via weathering and atmospheric deposition. Further research in

the HBN basins is needed to establish weathering rates, soil base-saturation status, and biomass budgets so that predictions can be made about stream water chemistry under various atmospheric deposition scenarios.

**Acknowledgments.** Funding for this study was provided by the U.S. Geological Survey. Terry Schertz, Mark Nilles, Keith Eshleman, and an anonymous reviewer provided helpful comments on the manuscript.

## References

- Aulenbach, B. T., R. P. Hooper, and O. P. Bricker, Trends in the chemistry of precipitation and surface water in a national network of small watersheds, *Hydrol. Process.*, 10, 151–181, 1996.
- Binkley, D., and T. C. Brown, Management impacts on water quality of forests and rangelands, *For. Serv. Gen. Tech. Rep. RM-239*, U.S. Dept. of Agric., Washington, D. C., 1993.
- Cleveland, W. S., Robust locally weighted regression and smoothing scatterplots, *J. Am. Stat. Assoc.*, 74, 829–836, 1979.
- Cobb, E. D., and J. E. Bieseker, *The National Hydrologic Benchmark Network*, U.S. Geol. Surv. Circ. 460-D, 1971.
- Driscoll, C. T., and R. Van Dreason, Seasonal and long-term temporal patterns in the chemistry of Adirondack lakes, *Water Air Soil Pollut.*, 67, 319–344, 1993.
- Driscoll, C. T., G. E. Likens, L. O. Hedin, J. S. Eaton, and F. H. Bormann, Changes in the chemistry of surface waters, *Environ. Sci. Technol.*, 23(2), 137–142, 1989.
- Fishman, M. J., and L. C. Friedman, *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments*, U.S. Geol. Surv. Tech. Water Resour. Invest., book 5, chap. A1, 1989.
- Fishman, M. J., J. W. Raese, C. N. Gerlitz, and R. A. Husband, U.S. Geological Survey approved inorganic and organic methods for the analysis of water and fluvial sediment, 1954–1994, U.S. Geol. Surv. Open File Rep. 94-351, 1994.
- Galloway, J. N., S. A. Norton, and M. R. Church, Freshwater acidification from atmospheric deposition of sulfuric acid: A conceptual model, *Environ. Sci. Technol.*, 17(11), 541A–545A, 1983.
- Gschwandtner, G., J. K. Wagner, and R. B. Husar, Comparison of historic SO<sub>2</sub> and NO<sub>x</sub> emission data sets, EPA-600/7-88-009a, U.S. Environ. Prot. Agency, Washington, D. C., 1988.
- Hedin, L. O., L. Granat, G. E. Likens, T. A. Buishand, J. N. Galloway, T. J. Butler, and H. Rodhe, Steep declines in atmospheric base cations in regions of Europe and North America, *Nature*, 367, 351–354, 1994.
- Helsel, D. R., and R. M. Hirsch, *Statistical Methods in Water Resources*, 522 pp., Elsevier, New York, 1992.
- Hirsch, R. M., J. R. Slack, and R. A. Smith, Techniques of trend analysis for monthly water quality data, *Water Resour. Res.*, 18(1), 107–121, 1982.
- Hornbeck, J. W., C. W. Martin, R. S. Pierce, F. H. Bormann, G. E. Likens, and J. S. Eaton, Clearcutting northern hardwoods: Effects on hydrologic and nutrient ion budgets, *For. Sci.*, 32, 667–686, 1986.
- Husar, R. B., T. J. Sullivan, and D. F. Charles, Historical trends in atmospheric sulfur deposition and methods for assessing long-term trends in surface water chemistry, in *Acidic Deposition and Aquatic Ecosystems*, edited by D. F. Charles, pp. 65–82, Springer-Verlag, New York, 1991.
- Kahl, J. S., S. A. Norton, C. S. Cronan, I. J. Fernandez, L. C. Bacon, and T. A. Haines, Maine, in *Acidic Deposition and Aquatic Ecosystems: Regional Case Studies*, edited by D. F. Charles, pp. 203–235, Springer-Verlag, New York, 1991.
- Kahl, J. S., T. A. Haines, S. A. Norton, and R. B. Davis, Recent trends in the acid-base status of surface waters in Maine, USA, *Water Air Soil Pollut.*, 67, 281–300, 1993.
- Kramer, J. R., A. W. Andren, R. A. Smith, A. H. Johnson, R. B. Alexander, and G. Oehlert, Streams and lakes, in *Acidic Deposition: Long-term Trends*, edited by J. H. Gibson, pp. 231–299, Natl. Acad., Washington, D. C., 1986.
- Lawrence, C. L., Streamflow characteristics at hydrologic benchmark stations, U.S. Geol. Survey Circ. 941, 1987.
- Likens, G. E., and F. H. Bormann, *Biogeochemistry of a Forested Ecosystem*, 159 pp., Springer-Verlag, New York, 1995.
- Likens, G. E., C. T. Driscoll, and D. C. Buso, Long-term effects of acid rain: Response and recovery of a forest ecosystem, *Science*, 272, 244–246, 1996.
- Lindberg, S. E., G. M. Lovett, D. D. Richter, and D. W. Johnson, Atmospheric deposition and canopy interactions of major ions in a forest, *Science*, 23, 141–145, 1986.
- Lovett, G. M., J. J. Bowser, and E. S. Edgerton, Atmospheric deposition to watersheds in complex terrain, *Hydrol. Processes*, 11(7), 645–654, 1997.
- Ludtke, A., and M. Woodworth, USGS blind sample project—monitoring and evaluating laboratory analytical quality, U.S. Geol. Surv. Fact Sheet FS-136-97, 1997.
- Lynch, J. A., and V. C. Bowersox, Effect of the 1990 amendments to the Clean Air Act, Title V on precipitation chemistry in the eastern United States, in *NADP Technical Committee Meeting*, p. 4, Natl. Atmos. Deposition Prog., Williamsburg, Va., 1996.
- Lynch, J. A., V. C. Bowersox, and C. Simmons, Precipitation chemistry trends in the United States: 1980–1993, summary report, Natl. Atmos. Deposition Prog., Williamsburg, Va., 1995a.
- Lynch, J. A., J. W. Grimm, and V. C. Bowersox, Trends in precipitation chemistry in the United States: A national perspective, 1980–1992, *Atmos. Environ.*, 29(11), 1231–1246, 1995b.
- Lynch, J. A., V. C. Bowersox, and J. W. Grimm, Trends in precipitation chemistry in the United States, 1983–1994—Analysis of the effects in 1995 of phase I of the Clean Air Act amendments of 1990, Title IV, U.S. Geol. Surv. Open File Rep. 96-0346, 1996.
- Mast, M. A., and J. T. Turk, Environmental characteristics and water quality of Hydrologic Benchmark Stations in the eastern United States, U.S. Geol. Surv. Circ., 1173-A, 1998.
- Meyers, T. P., and D. L. Sisterson, Network measurements of dry deposition of atmospheric pollutants, in *Acidic Deposition: State of Science and Technology*, edited by P. M. Irving, pp. 6.223–6.249, U.S. Natl. Acid Precip. Assess. Prog., Washington, D. C., 1991.
- Murdoch, P. S., and J. L. Stoddard, Chemical characteristics and temporal trends in eight streams of the Catskill Mountains, New York, *Water Air Soil Pollut.*, 67, 367–395, 1993.
- National Atmospheric Deposition Program, *Precipitation Chemistry in the United States*, Annual data summary, Coord. Off., Nat. Resour. Ecol. Lab., Colo. State Univ., Fort Collins, 1984–1996.
- Nizich, S. V., T. Pierce, and W. Hohenstein, National air pollutant trends, EPA-454/R-95-011, 1900–1994, U.S. Environ. Prot. Agency, Washington, D. C., 1995.
- Peden, M. E., Sampling, analytical and quality assurance protocols for the National Acid Deposition Program, in *Sampling and Analysis of Rain*, edited by S. A. Campbell, pp. 72–83, Am. Soc. of Test. Mat., Philadelphia, Pa., 1983.
- Ruess, J. O., and D. W. Johnson, *Acid Deposition and the Acidification of Soils and Waters*, 120 pp., Springer-Verlag, New York, 1986.
- Schertz, T. L., R. B. Alexander, and D. J. Ohe, The computer program Estimate Trend (ESTREND), a system for the detection of trends in water-quality data, U.S. Geol. Surv. Water Resour. Invest. Rep. 91-4040, 1991.
- Schertz, T. L., F. C. Wells, and D. J. Ohe, Sources of trends in water-quality data for selected streams in Texas, 1975–89 water years, U.S. Geol. Surv. Water Resour. Invest. Rep. 94-4213, 1994.
- Shortle, W. C., K. T. Smith, R. Minocha, G. B. Lawrence, and M. B. David, Acidic deposition, cation mobilization, and stress in healthy red spruce trees, *J. Environ. Qual.*, 26, 871–876, 1997.
- Smith, R. A., and R. B. Alexander, Evidence for acid-precipitation-induced trends in stream chemistry at hydrologic benchmark stations, U.S. Geol. Surv. Circ. 910, 1983.
- Stoddard, J. L., Trends in Catskill stream water quality: Evidence from historical data, *Water Resour. Res.*, 27(11), 2855–2864, 1991.
- Stoddard, J. L., and J. H. Kellogg, Trends and patterns in lake acidification in the state of Vermont: Evidence from the long-term monitoring project, *Water Air Soil Pollut.*, 67, 301–317, 1993.
- Stoddard, J. L., and P. S. Murdoch, Catskill Mountains, in *Acidic Deposition and Aquatic Ecosystems*, edited by D. F. Charles, pp. 237–271, Springer-Verlag, New York, 1991.
- Wesselink, L. G., J.-H. Meiwes, E. Matzner, and A. Stein, Long-term changes in water and soil chemistry in spruce and beech forests, Solling, Germany, *Environ. Sci. Technol.*, 29(1), 51–58, 1995.

D. W. Clow and M. A. Mast, Water Resources Division, U.S. Geological Survey, MS 415, Federal Center, Lakewood, CO 80227-0046. (dwcclow@usgs.gov)

(Received March 30, 1998; revised October 6, 1998; accepted October 6, 1998.)