Environ Monit Assess
DOI 10.1007/s10661-013-3256-6

Evaluation of stream chemistry trends in US Geological Survey reference watersheds, 1970–2010

M. Alisa Mast

Received: 9 January 2013 / Accepted: 11 May 2013
© Springer Science+Business Media Dordrecht (outside the USA) 2013

Abstract The Hydrologic Benchmark Network (HBN) is a long-term monitoring program established by the US Geological Survey in the 1960s to track changes in the streamflow and stream chemistry in undeveloped watersheds across the USA. Trends in stream chemistry were tested at 15 HBN stations over two periods (1970–2010 and 1990–2010) using the parametric Load Estimator (LOADEST) model and the nonparametric seasonal Kendall test. Trends in annual streamflow and precipitation chemistry also were tested to help identify likely drivers of changes in stream chemistry. At stations in the northeastern USA, there were significant declines in stream sulfate, which were consistent with declines in sulfate deposition resulting from the reductions in SO_2 emissions mandated under the Clean Air Act Amendments. Sulfate declines in stream water were smaller than declines in deposition suggesting sulfate may be accumulating in watershed soils and thereby delaying the stream response to improvements in deposition. Trends in stream chemistry at stations in other part of the country generally were attributed to climate variability or land disturbance. Despite declines in sulfate deposition, increasing stream sulfate was observed at several stations and appeared to be linked to periods of drought or declining streamflow. Falling water tables might have enhanced oxidation of organic matter in wetlands or pyrite in mineralized bedrock thereby increasing sulfate export in surface water. Increasing sulfate and nitrate at a station in the western USA were attributed to release of soluble salts and nutrients from soils following a large wildfire in the watershed.

Keywords Hydrologic Benchmark Network · Trends · Stream chemistry · Atmospheric deposition · Climate

M. A. Mast (✉)
US Geological Survey, Colorado Water Science Center,
Denver Federal Center,
Denver, CO 80225, USA
e-mail: mamast@usgs.gov

Introduction

The Hydrologic Benchmark Network (HBN) is a network of streams and rivers draining undeveloped watersheds that was established by the US Geological Survey (USGS) in the early 1960s. The main purpose of HBN is to provide a long-term database to track changes in the streamflow and water quality of undisturbed streams and rivers and to serve as reference for discerning natural from human-induced changes in river ecosystems. Hydrologic monitoring and assessment is central to the mission of the USGS and provides a scientific basis for effective management and protection of water resources across the nation (Hirsch et al. 2006). HBN has many characteristics of an effective water-quality monitoring program having maintained a long-term record of streamflow measurements and seasonal water-quality sampling as well as having stations in different geologic and climatic settings. The HBN data have been

Published online: 29 May 2013

important for evaluating the effectiveness of the Clean Air Act on forested ecosystems (Burns et al. 2006; Clow and Mast 1999; Murdoch and Shanley 2006; Smith and Alexander 1983), determining hydrologic and geochemical responses to variations in climate and acidic deposition (Lins 1985; Lins 1986) , estimating nutrient concentrations and yields for undeveloped watersheds (Clark et al. 2000a) , and identifying processes controlling solute concentrations in streams across the USA (Godsey et al. 2009). In recent years, HBN has invested resources in collecting ancillary information such as soil chemistry, aquatic biology, and continuous stream temperature, which will further enhance the value of the network.

The HBN streams are distributed across the USA and most drain areas with minimal human activities such as national parks, national forests, and nature preserves. The average size of HBN watersheds is 100 km^2, which is larger than typical research watersheds in which most ecosystem research is conducted (Murdoch et al. 2006). Most stations were established in the late 1960s and at its peak the network included 59 stations in 39 states. Due to cuts in program funding, the network was reevaluated in the early 2000s and downsized to the 37 stations that best meet the network criteria. Streamflow has been monitored continuously at each station since the network was established, but water-quality sampling has been more variable. Monthly to quarterly sampling was conducted until 1997 at which time water-quality sampling was suspended at many stations. Beginning in 2003, water-quality sampling was reinstated at a subset of the stations with a focus on sampling through the range in streamflow conditions with an emphasis on hydrologic events (Murdoch et al. 2006).

The original network design to study temporal trends was first evaluated in the early 1980s using 10–15 years of data from 47 HBN stations across the USA (Smith and Alexander 1983). The study reported small decreases in sulfate concentrations at stations in the northeast and increases at stations in the southeast and west that were attributed to regional trends in SO_2 emissions. At the time of the analysis, there were few long-term records of precipitation chemistry in the USA against which to compare stream chemical trends. Clow and Mast (1999) reevaluated trends at five of the HBN stations in the northeast with an additional 15 years of stream chemistry that overlapped with monitoring of precipitation chemistry conducted by the National Acid Deposition Program (NADP). Declines in stream sulfate at all five stations were similar in magnitude to declines in precipitation sulfate indicating streams were exhibiting a regional response to changes in atmospheric deposition. There were no detectable trends in acid-neutralizing capacity (ANC), which was attributed to delays in the recovery of soil base-saturation levels (Clow and Mast 1999). Murdoch and Shanley (2006) also assessed trends at three stations in the northeast but applied a new method to evaluate trends under different flow conditions. Consistent with previous studies, the authors reported declines in stream-water sulfate since the mid-1960s; however, the flow-specific analysis revealed that high-flow trends were better indicators of recent changes in water quality caused by reductions in acidic deposition (Murdoch and Shanley 2006).

This study reevaluates water-quality trends at selected stations in the HBN network over the period of record through 2010. Although there has been considerable focus on trends at HBN stations in the eastern USA, the HBN dataset has been extended another decade since the last analysis and nearly three decades since stations across the USA were evaluated. The operation of a successful long-term monitoring program includes not only continued collection of high-quality data records, but also periodic evaluation of the data to identify causes of environmental change (Lovett et al. 2007). To identify possible causes of change, trends in streamflow for the entire network and atmospheric deposition at nearby NADP stations also were examined. Since the last evaluation, there have been continued reductions in atmospheric emissions of sulfur and nitrogen because of the Clean Air Amendments enacted in 1990. Climate is another potentially important regional driver of chemical changes in streams and many regions of the country have experienced increases in air temperature since the 1970s (Tebaldi et al. 2012).

Methods

The HBN network currently includes 37 USGS streamflow-gaging stations (including one station in Alaska and one in Hawaii) many of which have been in operation since the mid-1960s (Fig. 1). This study focuses on trend analysis of water-quality data at the 15 HBN stations with the longest and most continuous water-quality records (Table 1). The period of record differed among the sites but most had water-quality data for a minimum of 30 years. Major ion and nutrient

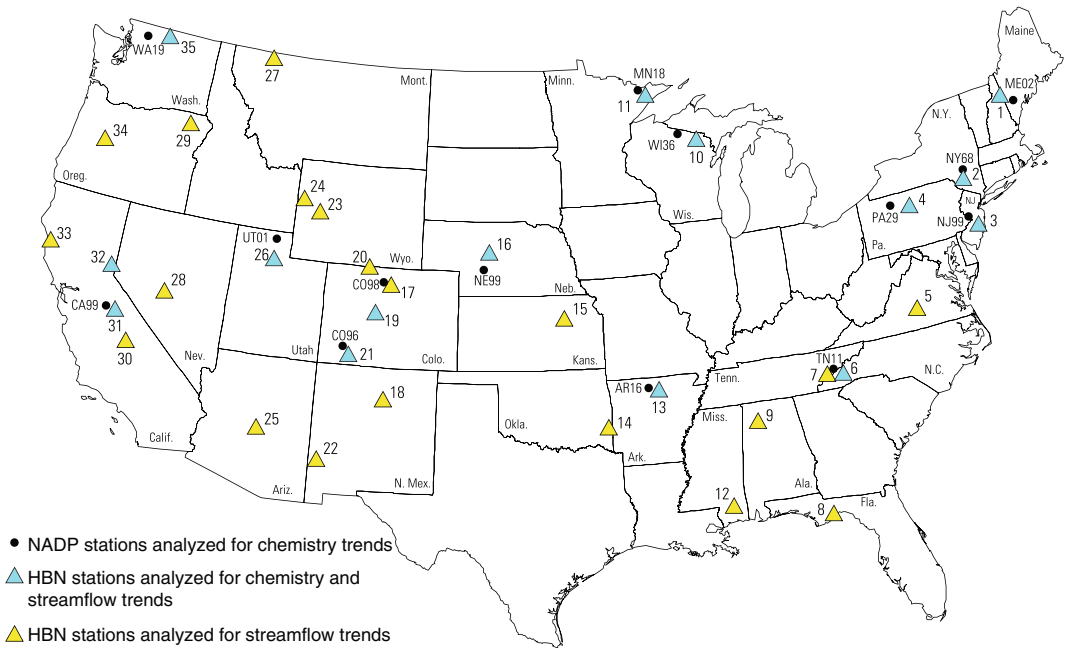

Fig. 1 Location of surface-water stations in the Hydrologic Benchmark Network (*HBN*) stations and collocated National Atmospheric Deposition Program (*NADP*) precipitation sites in the conterminous USA (site numbers from Table 1)

data were retrieved from the USGS National Water Information System (NWIS) at http://waterdata.usgs.gov/nwis for the period of record through 2010. In the NWIS database, water-quality data are stored using a system of five-digit parameter codes to identify the constituent measured and the units of measure (see http://waterdata.usgs.gov/usa/nwis/help?parameters_help). Constituents analyzed for this study are stored under single parameter codes with the exception of nitrate and ANC, which typically are stored under multiple codes. For example nitrate could be expressed in units of "mg/L as N" in one code (00618) and "mg/L as nitrate" in another code (71851). The multiple parameter codes for these two constituents were aggregated through a process of data conversions and combinations in order to obtain a single continuous record of concentrations for each constituent.

Temporal trends in stream chemistry were analyzed over two periods (1970–2010 and 1990–2010) using the USGS Load Estimator (LOADEST) model. LOADEST is a parametric technique that uses a regression model to predict loads based on discharge, time, and seasonal terms (Runkel et al. 2004). A statistically significant time term in the regression model indicates if there has been a linear change in the concentration-discharge relation over time. The trend in flow-adjusted concentration in microequivalent per liter year was computed from the coefficient of the linear time term (expressed as percentage change per year) times the mean concentration over the period of record tested. Validation of the regression model included checking the residuals for a linear fit, uniform scatter around the fit, and normality of the distribution. The LOADEST models were run using a version of the software adapted to run in the S-PLUS® software package. Because LOADEST was run on a daily time step, multiple event samples collected on the same day were averaged into a single concentration for the day.

Trends also were evaluated using the seasonal Kendall test (SKT), which is a nonparametric test that is useful for detecting monotonic trends in datasets that contain censored values, outliers, and missing data (Helsel and Hirsch 2002). The SKT uses Sen's slope estimator to determine the direction and slope of the trend. Although LOADEST and SKT yielded trends of similar magnitude and direction, the LOADEST results showed a greater number of statistically significant trends. This reflects the greater power of the parametric test at detecting trends provided the requirements of data normality are satisfied (Helsel and Hirsch 2002). Because model residuals from

Table 1 Active stations in the USGS Hydrologic Benchmark Network in the conterminous U.S and trends in streamflow

No.	Station name	USGS Station no.	Chemistry samples	Period of record	NADP station	Streamflow trends (% change per year)	
						1970–2010	1990–2010
1	*Wild River, Maine*	01054200	488	1970–2010	ME02	–	–
2	*Neversink River, New York*	01435000	781	1970–2010	NY68	–	–
3	*McDonalds Branch, New Jersey*	01466500	461	1970–2010	NJ99	–	–
4	*Young Womans Creek, Pennsylvania*	01545600	364	1970–2010	PA29	–	–
5	Holiday Creek, Virgina	02038850				–	–
6	*Cataloochee Creek, North Carolina*	03460000	181	1970–2003	TN11	–	−2.2
7	Little River, Tennessee	03497300				–	–
8	Sopchoppy River, Florida	02327100				–	–
9	Sipsey Fork, Alaska	02450250				–	–
10	*Popple River, Wisconsin*	04063700	426	1970–2010	WI36	−1.3	−2.9
11	*Kawishiwi River, Minnesota*	05124480	274	1970–2010	MN18	−1.5	–
12	Cypress Creek, Mississippi	02479155				−1.0	–
13	*North Sylamore Creek, Arkansas*	07060710	359	1970–2010	AR16	–	–
14	Kiamichi River, Oklahoma	07335700				–	−2.3
15	Kings Creek, Kansas	06879650				–	–
16	*Dismal River, Nebraska*	06775900	162	1973–2004	NE99	0.5	–
17	Big Thompson River, Colorado	402114105350101				–	–
18	Rio Mora, New Mexico	08377900				–	–
19	*Halfmoon Creek, Colorado*	07083000	365	1970–2002	CO98	–	–
20	Encampment River, Wyoming	06623800				–	–
21	*Vallecito Creek, Colorado*	09352900	431	1970–2010	CO96	–	–
22	Mogollon Creek, New Mexico	09430600				–	–
23	Pine Creek, Wyoming	09196500				–	–
24	Cache Creek, Wyoming	13018300				−1.0	–
25	Wet Bottom Creek, Arizona	09508300				–	–
26	*Red Butte Creek, Utah*	10172200	305	1970–2008	UT01	–	–
27	Swiftcurrent Creek, Montana	05014500				–	–
28	South Twin River, Nevada	10249300				–	–
29	Minam River, Oregano	13331500				–	–
30	Marble Fork of Kaweah, California	11206800				–	–
31	*Merced River, California*	11264500	443	1970–2010	CA99	–	–
32	*Sagehen Creek, California*	10343500	284	1970–2010	CA99	–	–
33	Elder Creek, California	11475560				–	–
34	Lookout Creek, Oregeon	14161500				–	–
35	*Andrews Creek, Washington*	12447390	201	1972–2010	WA19	–	–

Italicized stations analyzed for water quality and streamflow trends, all others analyzed for streamflow trends only

"–" Trend not statistically significant at p=0.05

LOADEST passed tests for normality for sulfate, base cations, and ANC, only the LOADEST trend results for these constituents are presented and discussed in this study. One exception was the LOADEST model for sulfate at Sagehen Creek which failed validation so the trends for SKT are presented instead.

In contrast to major constituents, nitrate could not be analyzed using LOADEST due to the high percentage of censored values. Nitrate trends were evaluated using a version of SKT for censored datasets (>5 %) and only for the period 1990–2010 due to multiple censoring levels in the early part of the record. For this study, four or six seasons per year were used depending on data availability at each station. If multiple samples per season occurred in the dataset, the sample closest to the center of the seasonal period was used in the analysis. The SKT for censored data does not allow flow adjustment of the concentration data so trends were evaluated on raw nitrate concentrations. SKT trends were evaluated using the computer program ESTREND (Schertz et al. 1991) adapted for the S-PLUS® software package.

Streamflow for all 35 HBN stations in the contiguous USA was obtained from the NWIS database. The Mann–Kendall test was used to test for monotonic trends in mean annual streamflow and Sen's slope estimator was used to determine trend direction and slope. Streamflow trends were tested over two periods, 1970–2010 and 1990–2010.

Precipitation chemistry data were obtained from the National Atmospheric Deposition Network (NADP) at http://nadp.sws.uiuc.edu/. The closest NADP station to each HBN station with a record that extended back to 1990 was selected for trend analysis (Fig. 1). Annual volume-weighted mean concentrations were obtained from the NADP website and concentrations were screened based on the NADP completeness criteria, which provide a measure of whether the available data are adequate to characterize the summary period. Cutoff values used in this study were ≥50 % for criteria 1 (% of period with valid samples) and 3 (% of total precipitation associated with valid samples), and >75 % for criterion 2 (% of period that precipitation amounts are available). A more complete description of completeness criteria is available at http://nadp.sws.uiuc.edu/documentation/completeness.asp. The Mann–Kendall test was used to test for monotonic trends in the screened annual concentrations and Sen's slope estimator was used to determine trend direction and slope. Trends were evaluated for sulfate, hydrogen ion, base cations (calcium plus magnesium), nitrate, and ammonium concentrations over the period 1990–2010. Trends for all tests and datasets were considered statistically significant if the p value was ≤0.05.

Analytical artifacts

It is generally assumed that temporal changes in stream chemistry reflect environmental change; however, concentration trends could potentially result from changes in sample collection and processing procedures as well as laboratory methods. For stations in the HBN, water-quality samples were collected using standard USGS protocols and procedures and changes in collection methods have been minor over the period of record (Wilde 2011). Some analytical methods used by USGS laboratories; however, have changed over time due to the development of new techniques or improvement of existing ones. Sulfate has the greatest potential for artifacts because the analytical method changed several times since the 1970s (Fishman et al. 1994). One documented issue with sulfate was a positive bias introduced by the turbidimetric method, which was used during the late 1980s. The bias was most pronounced in samples with low sulfate concentrations and appeared to be affected by factors such as color and turbidity (Mast and Turk 1999). The effect of this interference is illustrated in Fig. 2a where sulfate concentrations were elevated two- to threefold during the period this method was used. A possible reason for the strong bias at this station is that the

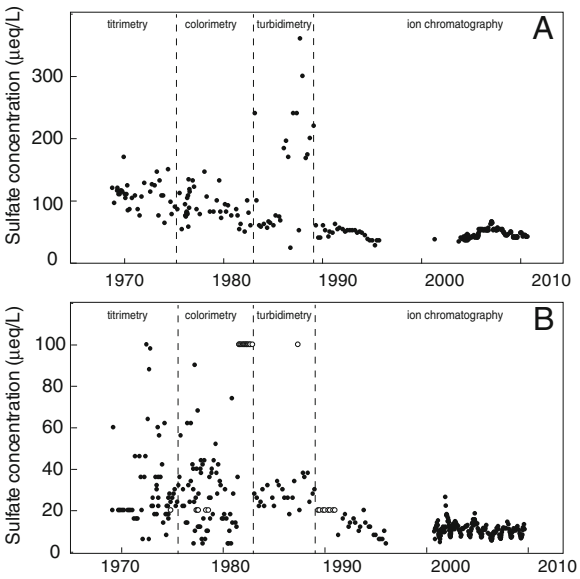

Fig. 2 Sulfate concentrations at **a** Kawishiwi River and **b** Merced River HBN stations compared to timing of different analytical methods used by USGS laboratories. *Open symbols* in **b** indicate concentrations were censored in database

water was strongly colored due to relatively high concentrations of dissolved organic carbon (>8 mg/L). Because the sulfate bias was not consistent among sites and could not easily be corrected, all sulfate concentrations analyzed by the turbidimetric method were excluded from the trend analysis. Another potential issue with sulfate was that analytical methods used prior to 1990 (titrimetric, colorimetric, and turbidimetric) appeared to produce concentrations with greater variability and potentially higher concentrations compared to those analyzed by ion chromatography. This was most notable in very dilute streams and is well illustrated in Fig. 2b by the time series of sulfate concentrations at an HBN station where sulfate concentrations are typically <1 mg/L. Interpretation of sulfate trends in dilute streams would clearly be complicated by the method changes so for sites with concentrations <2 mg/L, sulfate trends were only evaluated during the period when ion chromatography was used (1990–2010).

Results

Trends in precipitation chemistry and amount

Trends in precipitation chemistry were analyzed at the NADP station nearest to each of the 15 HBN stations analyzed for water-quality trends (Table 1). Although some NADP stations started operation in the mid-1980s, trends in this study were computed over the period 1990 to 2010 in order to test all stations over the same period of record. Results of the trend analysis are shown in Fig. 3 with sites roughly ordered from east to west across the figure. All NADP stations analyzed showed statistically significant declines in sulfate concentrations during 1990–2010, with the exception of stations in Nebraska (NE99) and California (CA99). Declines of similar magnitude in hydrogen ion concentrations also were detected. Fewer stations showed significant declines in nitrate concentrations and most were located in the eastern USA (Fig. 3). Trends in sulfate and hydrogen ion were greatest in the eastern USA, where powerplant SO_2 emissions have been reduced by as much as 70 % since 1990 as a result of the Clean Air Act Amendments of 1990 (Burns et al. 2011). Although decreases in precipitation sulfate also are evident at western NADP stations, the trends are much smaller because SO_2 emissions are substantially lower in the western USA. The decline in nitrate concentrations at NADP stations has been steepest over the last decade (2000–2010) compared to sulfate which has been declining steadily since 1990. NO_x emissions from powerplants also have declined because of the Clean Air Act Amendments although overall reductions have been more modest than for SO_2 because NOx also is derived from mobile and nonpoint sources such as motor vehicles and agriculture (Burns et al. 2011).

Trends in ammonium were both upward and downward but were statistically significant at four stations (Maine, ME02; Nebraska, NE99; Utah, UT08; and Washington, WA19) (Fig. 3). The upward trend at the Nebraska station was large compared to the other stations, which likely reflects its proximity to agricultural areas in the Midwest. Statistically significant trends in base cation concentrations were only detected at stations in New York (NY68) and Pennsylvania (PA29). The trends were decreasing and both stations, however, the trend magnitudes were small (<0.1 μeq/L/year). There were no detected trends in annual precipitation amount with the exception of the station near the Wild River (ME02), which showed a statistically significant (p=0.037) upward trend of 1.82 cm/year.

Trends in streamflow

Because changes in streamflow are an important influence on stream-water concentrations, all stations were tested (including those without chemistry) to help evaluate if regional trends in streamflow might have predominated over the period of study. HBN streams drain undeveloped watersheds so trends in streamflow should largely reflect variability in climate. Many of the stations in the northeast and Midwest had downward trends in annual streamflow; however, statistically significant trends were detected at only five stations during 1970–2010 and three stations during 1990–2010 (Table 1). The Popple River in Wisconsin (site 10) was the only site where a trend was detected during both periods of record. The trend was strongest during the more recent period (−2.9 % per year) and can be largely accounted for by lower than average flows over the last decade (2000–2010) (Fig. 4a). Annual runoff was positively correlated (r^2=0.29) with annual precipitation amount at the closest NADP station (WI36) and inversely correlated with annual air

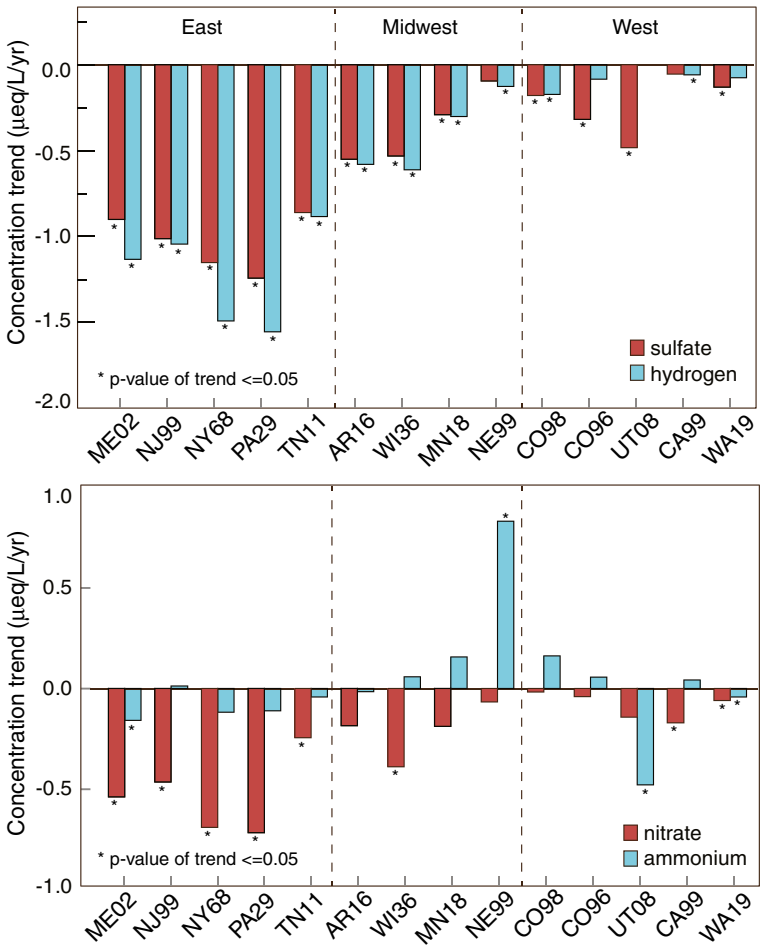

Fig. 3 Trends in sulfate, hydrogen ion, nitrate, and ammonium concentrations in precipitation at selected NADP stations across the USA for 1990–2010. Stations ordered roughly from east to west across the figure

temperature (r^2=0.24) indicating the combination of drier and warmer conditions likely contributed to declines in streamflow. Only one station, Dismal River (site 16) in the Nebraska Sand Hills, showed a statistically significant increase in streamflow (Fig. 4b). Other rivers in the Sand Hills region have shown similar upward trends for the period 1970 to 2000, which have been attributed to increases in precipitation and decreases in air temperature resulting in higher groundwater levels and increased streamflow (Chen et al. 2003). Studies of streamflow trends across the USA typically have reported increases in streamflow since the 1940s in most regions of the country (Lins 2005). An important aspect of the trends in the Lins (2005) study is that they appear to have occurred around 1970 as an abrupt rather than a gradual change. Because the streamflow analysis in this study starts around the time of this change, it makes sense that the increase observed nationwide was not detected in this study.

Trends in stream chemistry

Trend results for sulfate, base cations (calcium plus magnesium), and ANC from LOADEST for the 1970–2010 and 1990–2010 periods are presented in Tables 2, 3, and 4, and nitrate trends from SKT are in Table 5. The reader should be aware that a few stations have slightly shorter records than indicated in the trend tables including Cataloochee Creek, Dismal River, Halfmoon Creek, and Red Butte Creek (stations 6, 16, 19, and 26) (Table 1). For the period 1970–2010, statistically significant trends in sulfate concentrations were detected at 9 of the 12 stations tested (Table 2). All but one of the sulfate trends in the 1970–2010 period were downward and ranged in magnitude from

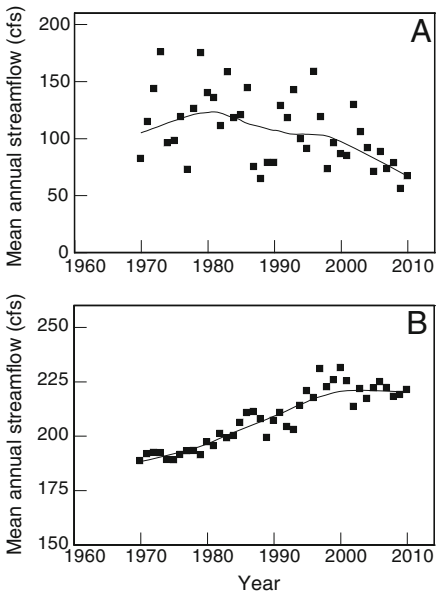

Fig. 4 Mean annual streamflow at **a** Popple River, Wisconsin, and **b** Dismal River, Nebraska. Trend lines generated by a locally weighted scatterplot smoothing function (LOWESS)

−0.4 to −2.0 μeq /L/year. Because of bias and variability introduced by changes in analytical methods discussed previously, caution should be taken in interpreting the long-term stream sulfate trends for these stations. For the more recent period (1990–2010), statistically significant trends were detected at 9 of 14 stations tested with LOADEST. Only at three stations in the northeast (Wild River, Neversink, Young Womans) was the magnitude and direction of the trend similar between the two periods. At two stations, McDonalds Branch and Popple River, the slope direction changed between the two periods switching from negative to positive.

For the period 1970–2010, statistically significant trends in base cation concentrations were detected at 12 of the 15 stations (Table 3). Similar to sulfate, most of the base cation trends during 1970–2010 were decreasing; however, at 10 stations the trend slopes were quite small (<0.3 % per year). Trends of very small magnitude, even if statistically significant, likely would not be environmentally relevant so they generally were not addressed in the discussion. For the more recent period (1990–2010), there were significant trends in base cations at 9 of 15 tested stations. Eight stations had statistically significant trends in both periods although at McDonalds Branch and Kawishiwi River the direction changed from negative to positive.

For the period 1970–2010, statistically significant trends in ANC concentrations were detected at 10 of the 14 stations (Table 4). Because McDonalds Branch is an acidic stream, trends were evaluated on hydrogen ion rather than ANC. All but one of the ANC trends during 1970–2010 were downward ranging from −0.4 to −6.5 μeq/L/year. The trend results for the more

Table 2 Trends in sulfate concentrations (μeq/L/yr) at 15 HBN stations during 1970–2010 and 1990–2010 computed using LOADEST and mean concentrations (μeq/L) for 1990–2010

Station name	Station no.	Trend 1970–2010	Trend 1990–2010	Mean conc.
Wild River	01054200	−1.0*	−0.8*	67
Neversink River	01435000	−2.0*	−2.3*	99
McDonalds Branch	01466500	−0.6*	1.4*	101
Young Womans Creek	01545600	−0.4*	−1.4*	152
Cataloochee Creek	03460000	0.1	−0.1	25
Popple River.	04063700	−0.7*	3.7*	123
Kawishiwi River	05124480	−1.5*	−0.1	49
North Sylamore Creek	07060710	−0.6*	−0.3	97
Dismal River	06775900	−1.2*	0.0	123
Halfmoon Creek	07083000	−0.3	0.1	96
Vallecito Creek	09352900	0.4*	2.5*	166
Red Butte Creek	10172200	−1.4	−23*	2,076
Merced River	11264500	–	0.1*	10
Sagehen Creek	10343500	–	0.0[a]	2
Andrews Creek	12447390	–	0.8*	24

*Trend significant at $p \leq 0.05$
"–" Not tested
[a]Trend computed with SKT

Table 3 Trends in calcium plus magnesium concentrations (μeq/L/yr) at 15 HBN stations during 1970–2010 and 1990–2010 computed using LOADEST and mean concentrations (μeq/L) for 1990–2010

Station name	Station no.	Trend 1970–2010	Trend 1990–2010	Mean conc.
Wild River	01054200	−1.4*	−0.4*	88
Neversink River	01435000	−0.8*	−0.3*	164
McDonalds Branch	01466500	−0.2*	0.8*	65
Young Womans Creek	01545600	−0.1	−0.2	278
Cataloochee Creek	03460000	−0.5*	−0.4*	75
Popple River.	04063700	3.5*	12*	1,747
Kawishiwi River	05124480	−0.2*	1.0*	279
North Sylamore Creek	07060710	−3.6*	−12*	2,677
Dismal River	06775900	−2.1*	−4.2	1,398
Halfmoon Creek	07083000	−0.9	−4.0	715
Vallecito Creek	09352900	−1.4*	2.4*	548
Red Butte Creek	10172200	−1.8	−37*	6,265
Merced River	11264500	−0.3*	0.3	111
Sagehen Creek	10343500	−3.3*	0.1	818
Andrews Creek	12447390	1.6*	1.1	397

*Trend significant at $p \leq 0.05$

recent period (1990–2010) showed significant trends at 4 of 14 stations. Only two sites showed statistically significant trends in both periods with the trend direction remaining the same at Dismal River but changing direction at Young Womans Creek. McDonalds Branch showed a statistically significant decrease in hydrogen ion (increase in pH) for 1970–2010 and no trend for 1990–2010.

Trends in nitrate concentrations were only tested with SKT because for most stations, a high percentage of concentrations were below laboratory reporting levels. In addition, the early part of the record often contained multiple reporting levels, so trends were only tested over the shorter period (1990–2010). Of the 10 stations tested, only three showed statistically significant trends in nitrate concentrations (Table 5).

Table 4 Trends in ANC concentrations (μeq/L/yr) at 15 HBN stations during 1970–2010 and 1990–2010 computed using LOADEST and mean concentrations (μeq/L) for 1990–2010

Station name	Station no.	Trend 1970–2010	Trend 1990–2010	Mean conc.
Wild River	01054200	−1.2*	−0.1	43
Neversink River	01435000	0.1	0.7*	45
McDonalds Branch[a]	01466500	−0.4*	−0.5	61
Young Womans Creek	01545600	−0.9*	1.0*	124
Cataloochee Creek	03460000	−0.8*	−0.9	95
Popple River.	04063700	2.3	7.4	1,519
Kawishiwi River	05124480	−0.2	−0.3	204
North Sylamore Creek	07060710	−3.6*	−4.5	2,584
Dismal River	06775900	−6.5*	−16*	1,548
Halfmoon Creek	07083000	0.6	−4.6*	660
Vallecito Creek	09352900	−2.1*	1.1	410
Red Butte Creek	10172200	1.6	1.9	4,509
Merced River	11264500	−0.7*	0.4	101
Sagehen Creek	10343500	−1.5*	0.4	1,047
Andrews Creek	12447390	1.0*	0.2	459

*Trend significant at $p \leq 0.05$
[a]Hydrogen ion tested instead of ANC

Table 5 Trends in nitrate concentrations (μeq/L/yr) at 15 HBN stations during 1990–2010 computed using the seasonal Kendall test and mean concentrations (μeq/L) for 1990−2010

Station name	Station no.	Trend 1990−2010	Mean conc.
Wild River	01054200	–	–
Neversink River	01435000	0.0	14.1
McDonalds Branch	01466500	–	–
Young Womans Creek	01545600	−0.7*	16.4
Cataloochee Creek	03460000	−0.4*	10.7
Popple River.	04063700	0.1	4.3
Kawishiwi River	05124480	0.1	2.1
North Sylamore Creek	07060710	0.0	4.3
Dismal River	06775900	0.3*	34.3
Halfmoon Creek	07083000	0.0	7.9
Vallecito Creek	09352900	0.0	8.4
Red Butte Creek	10172200	–	–
Merced River	11264500	–	–
Sagehen Creek	10343500	0.0	1.1
Andrews Creek	12447390	–	–

*Trend significant at $p \leq 0.05$
"–" Insufficient data for trend test

Young Womans Creek and Cataloochee Creek had decreases of −0.7 and −0.4 μeq/L/year, respectively during 1990–2010 and at the Dismal River an upward trend of 0.3 μeq/L/year was detected.

Discussion

Stream chemistry response to atmoshperic deposition

Declines in stream-water sulfate in the eastern USA have been clearly linked to declines in atmospheric deposition of sulfur since the 1980s due to reductions in SO_2 emissions resulting from Clean Air Act Amendments (Driscoll et al. 2003; Stoddard et al. 2003; Burns et al. 2006). The HBN results generally are consistent with this pattern with four of the five eastern stations showing downward sulfate trends for 1970–2010 and three of five showing downward trends for 1990–2010. Because of complications related to changing analytical methods and lack of deposition data prior to the late 1980s, this discussion focuses on sulfate trends in the more recent period. Figure 5 compares percent change in sulfate per year at the five eastern HBN stations with significant trends to deposition trends for 1990–2010. Trend magnitudes generally cannot be directly compared because evapotranspiration and dry deposition cause trends to be steeper in surface water than precipitation (Burns et al. 2006). For the three eastern stations with decreasing sulfate, percent declines in precipitation sulfate were greater than stream sulfate suggesting these watersheds are experiencing a lagged response to deposition (Stoddard et al. 2003). Accumulation of sulfate in watershed soils by processes such as adsorption on clays or incorporation in organic matter can reduce the rate of decline occurring in deposition (Stoddard et al. 2003). The Neversink River had the steepest decline in stream sulfate (−2.3 μeq/L/year), which was consistent with the average rate of decline of −2.3 μeq/L/year reported for other streams in the

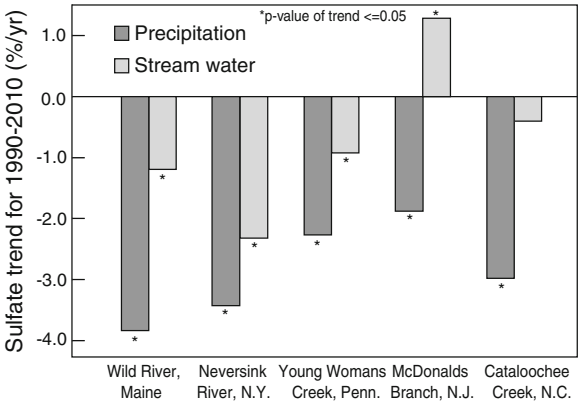

Fig. 5 Comparison of sulfate trends in precipitation and stream water at collocated HBN and NADP stations in the eastern USA, 1990–2010

Catskill Mountains where the Neversink River is located (Burns et al. 2006). In contrast, the trend at Wild River (−0.8 μeq/L/year) was lower than the average rate of decline of −1.6 μeq/L/year based on a regional assessment of streams and lakes in New England (Burns et al. 2011). Similarly, the trend at Young Womans Creek (−1.4 μeq/L/year) was lower than that average rate of −1.9 μeq/L/year for the Northern Appalachian region. The reason for the shallower trends at Wild River and Young Womans Creek is uncertain but could reflect the larger size of these watersheds compared to those used in the regional assessment.

All three of the northeastern sites showed slightly different responses in base cations and ANC. For 1990–2010, the Wild River had a downward trend in base cations but no significant trend in ANC. Neversink showed a downward trend in base cations and an upward trend in ANC, and Young Womans Creek had no trend in base cations but an upward trend in ANC. At the Wild River, the decrease in base cations of −0.4 μeq/L/year was half the decrease in sulfate of −0.8 μeq/L/year indicating other changes in stream chemistry may have occurred. Because no significant trend in ANC was observed, one possibility is that dissolved organic carbon (DOC) concentrations may have been increasing. Because a fraction of DOC typically is composed of organic anions, which can contribute 4 to 6 μeq/L per mg/L of carbon (Lawrence et al., 2011), it is plausible that an increase in DOC could account for part of the decrease in sulfate. Unfortunately, DOC data are not available at the site back to 1990; however, there is evidence that DOC has been increasing in streams throughout the northeast as acidic deposition declines (Driscoll et al. 2003; Burns et al. 2006), so this mechanism may be plausible for the Wild River. In the Neversink River, there was a small decrease in base cations but most of decline in sulfate was offset by the increase in ANC. Improvements in ANC indicate changes in the acid–base status of surface water and provide evidence that the Neversink River is recovering from decades of prolonged acidic deposition. This result is consistent with regional assessments in the Northern Appalachian Plateau and Adirondack Mountains, which show improvements in ANC in over 50 % of lakes and streams over the past two decades (Burns et al. 2011). In contrast to decreasing calcium and magnesium, sodium concentrations were increasing at the Neversink River by as much as 1.0 μeq/L/year, which is attributed to the use of road salt in the watershed based on similar trends in chloride (M. McHale, US Geological Survey, written communication, 2012). Young Womans Creek showed no trend in base cations and the decrease in sulfate was largely offset by an increase in ANC. Decreasing base cation concentrations has been reported for numerous lakes and streams in the northeast (Driscoll et al. 2003; Stoddard et al. 2003; Burns et al. 2006) and is attributed to reduced leaching of exchangeable cations in the soil in response to declines in atmospheric inputs of strong acid anions (sulfate and nitrate).

In contrast to the northeastern sites, Cataloochee Creek showed no trend in stream sulfate despite a decline of nearly 3 % per year in deposition. This likely reflects the higher sulfate adsorption properties of soils found in unglaciated areas of the eastern USA and is consistent with trends in stream sulfate reported for the Blue Ridge region by Stoddard et al. (2003). An unexpected result was the lack of a decreasing sulfate trend at McDonalds Branch in the New Jersey Pinelands where there have been dramatic reductions in acidic deposition. Stream water at this station is naturally acidic due to the sandy, base-poor soils characteristic of the Pinelands and the influence of wetlands, which cover over 15 % of the watershed. Despite a downward trend in sulfate deposition of −1.0 μeq/L/year, stream water showed an upward trend of 1.4 μeq/L/year from 1990 to 2010. A likely explanation for the lack of stream-water response is the presence of thick peat deposits in wetlands, which have a large capacity to store and cycle atmospherically deposited sulfate. Using sulfur isotopes, Mandernack et al. (2000) determined sulfur cycling varied greatly among different portions of the watershed and this had large effects on stream sulfate chemistry both spatially and seasonally. High rates of microbial sulfate reduction were measured in peats in headwater areas indicating some soils were sinks of sulfate, whereas further downstream, the peat could be a source of sulfate to stream water particularly in the late summer when falling water tables allowed oxidation of reduced sulfur pools (Mandernack et al. 2000). In fact, this oxidation mechanism may be a possible explanation for the increase in stream sulfate (and base cations) observed over the last two decades. Analysis of monthly streamflow records indicates that summer flows (July–September) have shown a statistically significant decline (−0.02 cfs/year, p=0.013) since 1970, suggesting wetland water tables might be falling during

summer months. A similar analysis of season precipitation amount does not show a trend suggesting that groundwater levels may be responding to other factors such as rising air temperatures, which could increase evaporation rates and lower water table levels even without a change in precipitation amount (Laudon et al. 2004).

In contrast to sulfate, relatively few trends were detected in stream-water nitrate concentrations with two stations in the east showing decreases and one station in the midwest showing an increase (Table 5). This result is not surprising considering forest nitrogen cycling is complex and a variety of factors including deposition, forest maturity, climate variability, and watershed disturbance history may influence stream nitrate concentrations (Aber et al. 2002). While declines in nitrate at Young Womans Creek and Cataloochee Creek (Table 5) were consistent with nitrate deposition trends (Fig. 3), the magnitude of the trend (% per year) was up to two times larger in stream water than precipitation. These results are consistent with other studies reporting greater than expected declines in stream-water nitrate in forested watersheds in the northeastern USA (Goodale et al. 2003; Judd et al. 2011). A recent study suggests that climate variability alone does not explain the trends and that recovery from past logging may be the main factor (Bernal et al. 2012). Although forests in both HBN watersheds have been logged to varying degrees (Mast and Turk 1999), with the limited datasets available for these watersheds, it is not possible to quantify the effect of past land-use change on the nitrate trends at these sites. At the Dismal River station in central Nebraska, nitrate concentrations were found to be increasing rate of 0.9 % per year. At the closest NADP station (NE99), nitrate has actually declined since 2000, but ammonium concentrations have increased appreciably at a rate of over 2.0 % per year. Increases in ammonium concentration in precipitation have been noted across the USA (Lehmann et al. 2007) but are particularly notable in the central and upper Midwest where agriculture is most concentrated. Because ammonium is largely converted to nitrate in soils, the trend in stream nitrate may indicate the watershed is responding to enhanced nitrogen deposition. Other land-use activities that also may affect stream nitrate include livestock grazing, which is common throughout the watershed, and a small amount of hay production (Clark et al. 2000b).

Stream chemistry response to climate variability and land disturbance

It was anticipated that most stream chemistry trends would be linked to changes in atmospheric deposition, given that the HBN watersheds are largely undeveloped and few trends were detected in annual streamflow. One notable exception with respect to hydrologic change was the Dismal River (site 16) in the Sand Hills of Nebraska, which showed an increase in streamflow of 17 % during 1977 to 1999 due to subtle shifts in climate that increased infiltration to the groundwater system (Chen et al. 2003). In addition to an increase in nitrate, there were other water-quality trends at this station including a decrease in sulfate over the longer period and ANC in both periods (Tables 2 and 4). Sulfate concentrations remained unchanged at the closest NADP station (NE99) suggesting the stream-water trend was not driven by changes in deposition. However, the trend in deposition was for the later period (1990–2010), which did not coincide with the period that the stream sulfate trend was detected. There was a downward shift in stream-water sulfate concentrations around 1990 (Fig. 6a), at the time ion chromatography was approved as the standard method for sulfate analyses. Because trends were evaluated on flow-adjusted concentrations, which minimizes the influence of variations in streamflow, and because the concentration shift was abrupt relative to the trend in streamflow, the trend in sulfate at this station may reflect the change in analytical method rather than the shift in climatic conditions. The cause of the downward trend in ANC is uncertain. Although increased streamflow generally decreases concentrations of weathering-derived constituents, flow adjustment prior to trend analysis should have corrected for this effect. One possible explanation is that climatic shifts have caused the relation between flow and concentration to change through time, which cannot be evaluated by the statistical methods used in this study (Hirsch et al. 2010).

A few stations (Popple River, Vallecito Creek, and Andrews Creek) showed significant increases in stream sulfate concentrations (0.7 to 3.7 μeq/L/year) despite the declines in sulfate deposition that occurred in most regions of the USA. Sulfate concentrations in the Popple River (site 10) increased by 3.7 μeq/L/year over the more recent period (1990–2010) (Fig. 6b) at the same time that sulfate deposition was declining by −0.5 μeq/L/year. Kerr et al. (2011) studied catchments

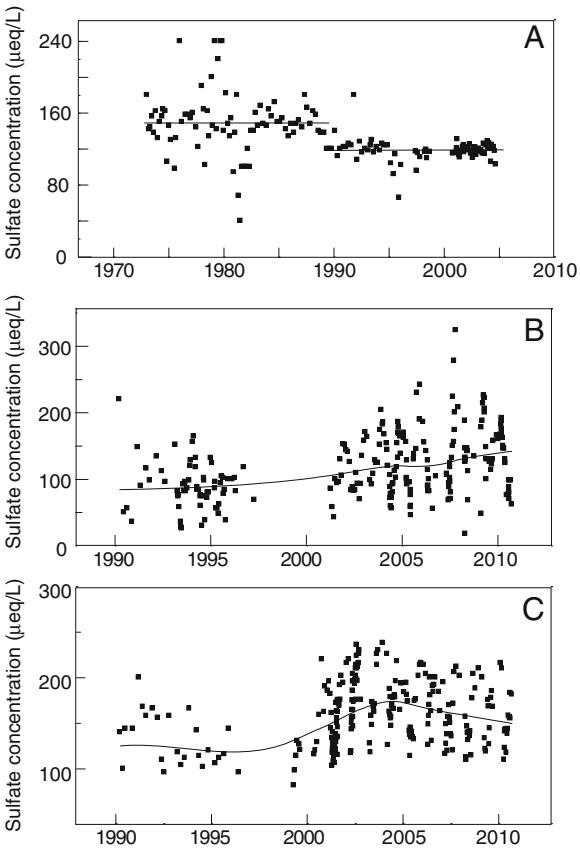

Fig. 6 Stream-water sulfate concentrations from 1990 to 2010 at **a** Dismal River, Nebraska, **b** Popple River, Wisconsin, and **c** Vallecito Creek, Colorado. Trend lines were generated by a locally weighted scatterplot smoothing function (LOWESS)

in northeastern USA and southeastern Canada and found that increases in sulfate in many streams could be explained by seasonal drying, particularly those with a large percentage of wetlands or saturated areas. Eimers et al. (2007) showed that extended dry periods, particularly in summer, caused a lowering of water tables and oxidation of organically bound sulfur in wetlands, which can be flushed to streams when streamflows recover in the following fall and winter. This mechanism might be plausible for the Popple River given that wetlands cover 30 % of the watershed (Mast and Turk 1999) and could contain a large pool of organically bound sulfur that has accumulated over decades of acidic deposition. Annual streamflow also declined in the Popple River during the period of increasing sulfate and there were indications of a shift towards drier warmer summers, particularly in the last decade when the highest sulfate concentrations were observed (Fig. 6b). For example, extended dry periods in late summer were more common over the last decade with 6 of the 10 lowest September flows on record (1964–2010) occurring since 1998. Air temperatures also were increasing with 7 of the 10 warmest mean September air temperatures on record (1968–2010) occurring since 1998 (station STAMBAUGH 2 SSE, http://www.wrcc.dri.edu/). The cause of the increase in sulfate in the Popple River is uncertain, although it seems plausible that climate variability may have played a role in offsetting any stream response to reductions in sulfate deposition.

Vallecito Creek (site 21) drains high-elevation mountainous terrain and, in contrast to the Popple River, has thin rocky soils with sparse discontinuous wetlands (Clark et al. 2000b). Most of the sulfate increase in Vallecito Creek occurred in the early 2000s then leveled off or declined slightly following a period of regional drought that persisted through 2002 (Mast et al. 2011). Because the bedrock in some areas of the watershed has undergone weak sulfide mineralization, stream-water sulfate is largely derived from geologic sources, specifically pyrite weathering, rather than deposition (Mast et al. 2011). Similar increases in surface-water sulfate were reported for several high-elevation lakes in Colorado with the sharpest increases after 1995 (Mast et al. 2011). Interestingly, three of the lakes are located in the headwaters of Vallecito Creek, suggesting the driver is affecting stream chemistry throughout the watershed and is not just localized in one area. Todd et al. (2012) also observed increases in sulfate (and zinc) concentrations up to 400 % since the mid-1980s in an alpine stream in Colorado that drains an unmined area with extensive pyrite mineralization. Neither study reported trends in precipitation or streamflow, but air temperature was found to have increased by as much as 1.0 °C per decade since the 1980s leading to the conclusion that climate was the driver. Although the exact mechanism is uncertain, warmer temperatures could enhance evapotranspiration reducing recharge rates and causing water tables to fall. If the water table falls, a larger subsurface rock volume becomes exposed to oxygen, potentially allowing more total sulfide oxidation and elevated sulfate and metal concentrations in groundwater discharging to lakes and streams (Mast et al. 2011; Todd et al. 2012). If climate change leads to greater frequency of warm, dry summers, water-quality degradation in mineralized areas could

progress to the point at which downstream aquatic communities are affected (Todd et al. 2012).

Another high-elevation watershed, Andrews Creek (site 32) in Washington, also showed increasing sulfate from 1990 to 2010, although samples are largely lacking from the middle part of the record so the exact timing of the increase is not well constrained (Fig. 7). The increase in sulfate occurred following a large wildfire (Farewell Fire), which burned much of the watershed in the summer of 2003 (Bureau of Reclamation 2008). During the following summer, a series of thunderstorms triggered landslides in the watershed and deposited large amounts of sediment and woody debris in the channel (R. Drzymkowski, US Geological Survey, written communication, 2012). Other chemical changes were observed following the fire including an increase in nitrate, peaking in February 2006 at 0.5 mg/L as N (36 μeq/L) (Fig. 7). Elevated nitrate concentrations are commonly reported following wildfire and generally are ascribed to the combination of reduced uptake by vegetation and increased soil nitrification of ammonium released during burning of organic matter (Ranalli 2004; Certini 2005). Nitrate concentrations in Andrews Creek remained elevated for about 5 years following the fire and seasonally were highest in winter base flow similar to results reported for a watershed in Glacier National Park that also burned in 2003 (Mast and Clow 2008). The fire in Andrews Creek had little effect on other major constituents with the exception of sulfate and chloride, which has been attributed to accumulation of soluble salts in the ash due to oxidation of soil organic matter or release from burning of plant tissue (Murphy et al. 2006). Although there were no significant trends in annual streamflow for 1990 to 2010, there appeared to be increases in streamflow during winter and the early snowmelt period (April) after the fire (Fig. 7). Winter flows might be enhanced due to reductions in intercepted snow sublimation with decreasing canopy coverage (Westerling et al. 2006).

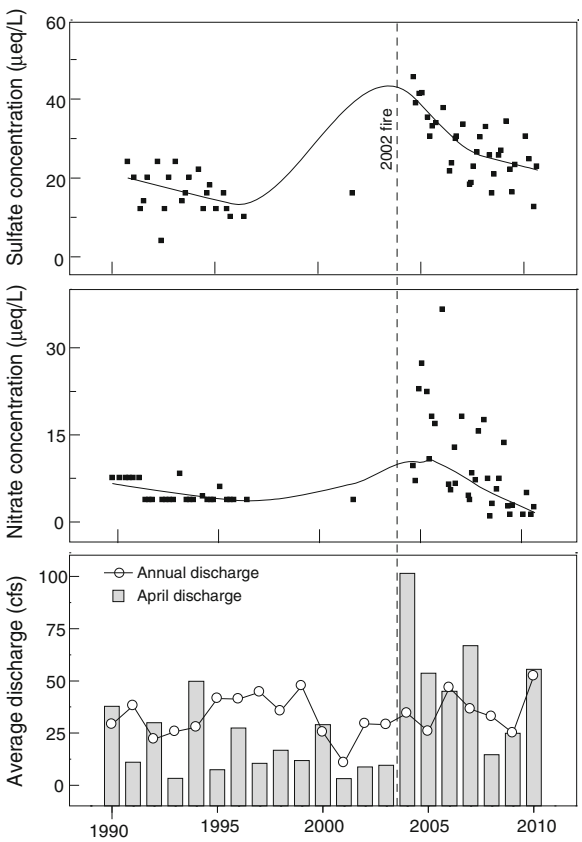

Fig. 7 Concentrations of **a** sulfate and **b** nitrate, and **c** annual and April discharge at Andrews Creek station in Washington. The *dashed line* represents the date of a wildfire that burned most of the watershed

Red Butte Creek (site 26) in Utah showed a downward trend in sulfate during the most recent period (1990–2010). Although this is consistent with the downward trend in deposition at UT01, sulfate in Red Butte Creek averages 2,076 μeq/L (100 mg/L), which is more than 2 orders of magnitude higher than sulfate in deposition (13 μeq/L) clearly ruling this out as the source of the trend. The stream-water trend was largely driven by elevated concentrations in the early 1990s, which coincided with an extended period of drought that persisted from 1988 to 1992. Mean annual streamflow in all 5 years ranked among the 10 lowest on record for 1964–2010 with 1990 having the lowest mean annual streamflow (1.12 cfs) of the entire 47-year record. Although the statistical models correct for hydrologic conditions, flow-adjusted concentrations were clearly elevated in the early 1990s suggesting the relation between concentration and flow had shifted during this extended dry period. The downward trend in sulfate was largely balanced by the downward trend in base cations (Table 3), which is consistent with weathering of gypsum in the underlying marine sedimentary rocks (Ehleringer et al. 1992) as the controlling process. In contrast, there was little change in ANC concentrations during the drought years and hence no trend was detected in ANC during 1990–2010 (Table 4).

Conclusions

This study evaluates stream chemistry trends at stations in the Hydrologic Benchmark Network, which was established by the USGS to provide a long-term database to track changes in the streamflow and water quality of undisturbed streams and rivers. Operation of a successful long-term monitoring network not only includes continuous collection of high-quality data but also periodic evaluation of these datasets, which was a major impetus for this study. Although the network has been evaluated for trends in the past, the dataset has been extended another decade since the last analysis and nearly three decades since stations across the country were evaluated. A potential challenge in using historical water-quality records for trend analysis is that collection and analytical methods are not always consistent over the entire period of record. For the HBN records, analytical methods used for sulfate likely introduced a positive bias and greater variability in sulfate concentrations prior to 1990 and care should be taken in application and interpretation these data. Several changes in laboratory reporting levels also complicated evaluation of trends in stream-water nitrate concentrations.

Observed trends in stream chemistry at HBN stations were attributed to both regional drivers such as changes in atmospheric deposition and local factors such as watershed characteristics and land disturbance events. In the northeast, there were significant declines in stream sulfate consistent with declines in sulfate deposition resulting from the reductions in SO_2 emissions mandated under the Clean Air Act Amendments. Sulfate declines in streams were smaller than in deposition suggesting sulfate may be accumulating in watershed soils and thereby delaying the stream response to improvements in acidic deposition. An unexpected result was the upward trend in sulfate at McDonalds Branch in the New Jersey Pinelands where reductions in sulfate deposition have been considerable. Watershed characteristics appear to provide a likely explanation. Thick peat deposits in extensive wetlands have a large capacity to store and release atmospherically deposited sulfate thus buffering the response of the stream to changing inputs of sulfate. Trends in stream chemistry at stations in other parts of the country generally were attributed to climate variability or changes in land disturbance. Increasing stream sulfate occurred at stations in the Midwest and Rocky Mountains and appeared to be linked to periods of drought. Falling water tables might have enhanced oxidation of organic matter in wetlands or pyrite in mineralized bedrock, thereby increasing sulfate concentrations in surface water. Increasing sulfate and nitrate at the Andrews Creek station in Washington were attributed to release of soluble salts and nutrients from soils following a large wildfire that burned much of the watershed in 2002.

Acknowledgments This work was supported by the Hydrologic Network and Analysis Program of the US Geological Survey. Special thanks to Jenn Moore, Colorado Mountain College, for assistance with data compilation and trend analysis. The authors also thank Mike McHale and two anonymous reviewers for their helpful comments on the manuscript.

References

Aber, J. D., Holmes, R. T., Freuder, R. J., Goodale, C. L., Ollinger, S. V., Driscoll, C. T., et al. (2002). Inorganic nitrogen losses from a forested ecosystem in response to physical, chemical, biotic, and climatic perturbations. *Ecosystems, 5*, 648–658.

Bernal, S., Hedin, L. O., Likens, G. E., Gerber, S., & Buso, D. C. (2012). Complex response of the forest nitrogen cycle to climate change. *Proceedings of the National Academy of Sciences, 109*(9), 3406–3411.

Bureau of Reclamation (2008). Methow subbasin geomorphic assessment, Okanogan County, Washington. http://www.usbr.gov/pn/programs/fcrps/thp/ucao/methow/geomorphicassessment/geomorph2008.pdf. Accessed May 2013.

Burns, D. A., McHale, M. R., Driscoll, C. T., & Roy, K. M. (2006). Response of surface water chemistry to reduced levels of acid precipitation: comparison of trends in two regions of New York. *Hydrological Processes, 20*, 1611–1627.

Burns, D. A., Lynch, J. A., Cosby, B. J., Fenn, M. E., Baron, J. S., & US EPA Clean Air Markets Div. (2011). *National acid precipitation assessment program report to congress 2011: an integrated assessment*. Washington, DC: National Science and Technology Council. 114 p.

Certini, G. (2005). Effects of fire on properties of forest soils: a review. *Oecologia, 143*, 1–10.

Chen, X., Rowe, C., Hu, Q., & Anderson, M. (2003). Geological and climatic controls on streamflows in the Nebraska Sand Hills. *Journal of the American Water Resources Association, 39*, 217228.

Clark, G. M., Mueller, D. K., & Mast, M. A. (2000a). Nutrient concentrations and yields in undeveloped basins of the United States. *Journal of the American Water Resources Association, 36*, 849–860.

Clark, M.L., Eddy-Miller, C.A., & Mast, M.A. (2000b). Environmental characteristics and water quality of hydrologic benchmark network stations in the west-central United

States, 1963–95. US Geological Survey Circular 1173-C, 115 p.

Clow, D. W., & Mast, M. A. (1999). Long-term trends in stream water and precipitation chemistry at five headwater basins in the northeastern United States. *Water Resources Research, 35*(2), 541–554.

Driscoll, C. T., Driscoll, K. M., Roy, K. M., & Mitchell, M. J. (2003). Chemical response of lakes in the Adirondack Region of New York to declines in acidic deposition. *Environmental Science & Technology, 37*(10), 2036–2042.

Ehleringer, J. R., Arnow, L. A., Arnow, T., McNulty, I. B., & Negus, N. C. (1992). Red Butte Canyon Research Natural area-history, flora, geology, climate, and ecology. *Great Basin Naturalist, 52*(2), 95–121.

Eimers, M. C., Watmough, S. A., & Buttle, J. M. (2007). Drought-induced sulphate release from a wetland in south-central Ontario. *Environmental Monitoring and Assessment, 127*, 399–407.

Fishman, M. J., Raese, J. W., Gerlitz, C. N., & Husband, R. A. (1994). US Geological Survey approved inorganic and organic methods for the analysis of water and fluvial sediment, 1954–94. US Geological Survey Open-File Report 94–351, 55 p.

Godsey, S., Kirchner, J. W., & Clow, D. W. (2009). Concentration-discharge relationships reflect chemostatic characteristics of catchments. *Hydrological Processes, 23*, 1844–1864.

Goodale, C. L., Aber, J. D., & Vitousek, P. M. (2003). An unexpected nitrate decline in New Hampshire Streams. *Ecosystems, 6*, 75–86.

Helsel, D. R., & Hirsch R. M. (2002). Statistical methods in water resources. Techniques of Water-Resources Investigations, Book 4, chapter A3. US Geological Survey, 522 p.

Hirsch, R. M., Hamilton, P. A., & Miller, T. L. (2006). US Geological Survey perspective on water-quality monitoring and assessment. *Journal of Environmental Monitoring, 8*, 512–518.

Hirsch, R. M., Moyer, D. L., & Archfield, S. A. (2010). Weighted regressions on time, discharge, and season (WRTDS), with an application to Chesapeake Bay River inputs. *Journal of the American Water Resources Association, 46*, 857–880.

Judd, K. E., Likens, G. E., Buso, D. C., & Bailey, A. S. (2011). Minimal response in watershed nitrate export to severe soil frost raises questions about nutrient dynamics in the Hubbard Brook experimental forest. *Biogeochemistry, 106*, 443–459.

Kerr, J. G., Eimers, M. C., Creed, I. F., Adams, M. B., Beall, F., Burns, D., et al. (2011). The effect of seasonal drying on sulphate dynamics in streams across southeastern Canada and the northeastern. *Biogeochemistry, 10*, 1–17.

Laudon, L., Dillon, P. J., Eimers, M. C., Semkin, R. G., & Jeffries, D. S. (2004). Climate-induced episodic acidification of streams in central Ontario. *Environmental Science & Technology, 38*, 6009–6015.

Lawrence, G. B., Simonin, H. A., Baldigo, B. P., Roy, K. M., & Capone, S. B. (2011). Changes in the chemistry of acidified Adirondack streams from the early 1980s to 2008. *Environmental Pollution, 159*(10), 2750–2758.

Lehmann, C. M. B., Bowersox, V. C., Larson, R. S., & Larson, S. M. (2007). Monitoring long-term trends in sulfate and ammonium in US precipitation: results from the National Atmospheric Deposition Program/National Trends Network. *Water, Air, and Soil Pollution Focus, 7*, 59–66.

Lins, H. F. (1985). Interannual streamflow variability in the United States based on principal components. *Water Resources Research, 21*, 691–701.

Lins, H. F. (1986). Recent patterns of sulfate variability in pristine streams. *Atmospheric Environment, 20*, 367–375.

Lins, H.F. (2005). Streamflow trends in the United States from the National Streamflow Information Program. US Geological Survey Fact Sheet 2005–3017, 4 p.

Lovett, G. M., Burns, D. A., Driscoll, C. T., Jenkins, J. C., Mitchell, M. J., Rustad, L., et al. (2007). Who needs environmental monitoring? *Frontiers in Ecology and the Environment, 5*, 253–260.

Mandernack, K. W., Lynch, L., Krouse, H. R., & Morgan, M. D. (2000). Sulfur cycling in wetland peat of the New Jersey Pinelands and its effect on stream water chemistry. *Geochimica et Cosmochimica Acta, 64*, 3949–3964.

Mast, M. A., & Clow, D. W. (2008). Effects of 2003 wildfires on stream chemistry in Glacier National Park, Montana. *Hydrological Processes, 22*, 5013–5023.

Mast, M. A., & Turk, J. T. (1999). Environmental characteristics and water quality of hydrologic benchmark network stations in the Midwestern United States, 1963–95. US Geological Survey Circular 1173-B, 130 p.

Mast, M. A., Turk, J. T., Clow, D. W., & Campbell, D. H. (2011). Response of lake chemistry to changes in atmospheric deposition and climate in three high-elevation wilderness areas of Colorado. *Biogeochemistry, 103*, 27–43.

Murdoch, P. S., & Shanley, J. B. (2006). Flow-specific trends in river-water quality resulting from the effects of the Clean Air Act in three mesoscale, forested river basins in the northeastern United States through 2002. *Environmental Monitoring and Assessment, 120*, 1–25.

Murdoch, P.S., McHale, M.R., Mast, M.A., & Clow, D.W. (2006). The US Geological Survey Hydrologic Benchmark Network. US Geological Survey Fact Sheet 2005–3135, 6 p

Murphy, J. D., Johnson, D. W., Miller, W. W., Walker, R. F., Carroll, E. F., & Blank, R. R. (2006). Wildfire effects on soil nutrients and leaching in a Tahoe basin watershed. *Journal of Environmental Quality, 35*, 479–489.

Ranalli, A.R. (2004). A summary of the scientific literature on the effects of fire on the concentration of nutrients in surface waters. US Geological Survey Open-File Report 2004–1296, 23 p.

Runkel, R.L., Crawford, C.G., & Cohn, T.A. (2004). Load Estimator (LOADEST): a FORTRAN program for estimating constituent loads in streams and rivers. US Geological Survey Techniques and Methods Book 4, Chapter A5, 69 p.

Schertz, T.L., Alexander, R.B., & Ohe, D.J. (1991). The computer program estimate trend (ESTREND), a system for the detection of trends in water-quality data. US Geological Survey Water-Resources Investigations Report 91–4040, 63 p.

Smith, R.A., & Alexander, R.B. (1983). Evidence for acid-precipitation-induced trends in stream chemistry at hydrologic bench-mark stations. US Geological Survey Circular 910, 12 p.

Stoddard, J.L., Kahl, J.S., Deviney, F.A. et al. (2003). Response of Surface Water Chemistry to the Clean Air Act Amendments of 1990. USEPA, Research Triangle Park, EPA/620/R-03/001NC.

Tebaldi, C., Adams-Smith, D., Heller, N. (2012). The heat is on: U.S temperature trends. Climate Central. http://

www.climatecentral.org/wgts/heat-is-on/HeatIsOnReport.pdf. Accessed January 2013.

Todd, A.S, Manning, A.H., Verplanck, P.L., Crouch, C., McKnight, D.M., & Dunham, R. (2012). Climate-change-driven deterioration of water quality in a mineralized watershed. Environmental Science & Technology. doi:10.1021/es3020056

Westerling, A. L., Hidalgo, H. G., Cayan, D. R., & Swetnam, T. W. (2006). Warming and earlier spring increase western US forest wildfire activity. *Science, 313*, 940–943.

Wilde, F.D. (2011). Water-quality sampling by the US Geological Survey: standard protocols and procedures. US Geological Survey Fact Sheet 2010–312, 2 p.