TRENDS IN PRECIPITATION AND STREAM-WATER CHEMISTRY IN THE NORTHEASTERN UNITED STATES, WATER YEARS 1984—96

By D.W. Clow and M.A. Mast

Trends in precipitation and stream-water chemistry during water years 1984–96 were examined at eight precipitation monitoring sites and five nearby streams operated by the U.S. Geological Survey in the northeastern United States. The statistical analyses indicate the following:

- Stream-water sulfate (SO_4) concentrations decreased at seven of eight precipitation monitoring sites and in each of five streams.
- Calcium plus magnesium (Ca + Mg) concentrations decreased at seven of eight precipitation monitoring sites and in three of five streams.
- Precipitation acidity decreased at five of eight precipitation monitoring sites, but alkalinity increased in only one stream.

These results indicate that decreases in atmospheric deposition of SO_4 have resulted in decreased precipitation acidity. The chemical response of stream water to changes in precipitation chemistry was complex. Decreases in stream-water SO_4 concentrations generally matched decreases of precipitation SO_4. In stream water, increases in alkalinity were uncommon because decreases in SO_4 concentrations often were accompanied by decreases in Ca + Mg concentrations. The decreases in Ca + Mg concentrations might be related to depletion of base cations from soil caused by long-term exposure to acidic deposition. Increases in stream-water alkalinity might not occur until rates of acidic deposition are reduced to substantially less than the rate of cation resupply by weathering and atmospheric deposition. In areas where forests are aggrading, recovery of stream-water alkalinity will be delayed further because of the acidifying effect of biomass accumulation.

Introduction

Ecosystems in the northeastern United States have been exposed to elevated levels of acidic deposition since the early part of the 20th century (Gschwandtner and others, 1988). The main components of acidic deposition are sulfuric and nitric acids, which are derived primarily from sulfur dioxide (SO_2) and nitrogen oxide (NO_x) gases created during fossil-fuel combustion. Numerous studies report that soil and surface water in many parts of the northeastern United States have been affected 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 soil-exchange sites (Ruess and Johnson, 1986). As base cations become depleted from the soil-exchange pool, the alkalinity of streams and lakes decreases, and surface water becomes more susceptible to episodic acidification during snowmelt and storms (Stoddard, 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 and sugar maple forests in the northeastern United States (Long and others, 1997; Shortle and others, 1997).

Emissions of SO_2 and NO_x increased substantially during the 20th century and peaked in the 1970's (fig. 1). Since then, SO_2 emissions have decreased and NO_x emissions have leveled off. These changes in emissions have occurred mostly because of economic recessions in the mid- to late 1970's and early 1990's and emissions controls mandated by the Clean Air Act of 1970 (Nizich and others, 1995). The overall decline in emissions of acid precursors (SO_2 and NO_x) during the past two decades has resulted in a decrease in strong-acid anion deposition during that period (Lynch and others, 1996). At some point, soils, lakes, and streams should begin to recover from their long term exposure to acidic deposition. Conceptual

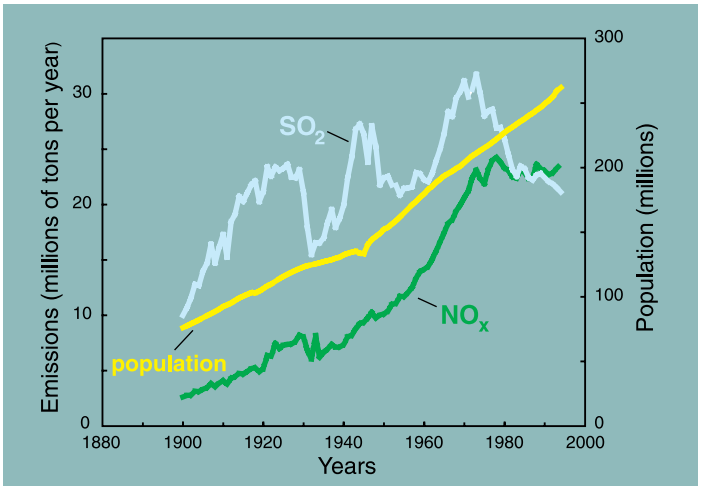


Figure 1. Trends in population, sulfur dioxide (SO_2), and nitrogen oxide (NO_x) emissions in the United States for 1900 to 1995. Source: Nizich and others (1995).

Figure 2. Tributary stream in Wild River, Maine, Hydrologic Benchmark Network basin.

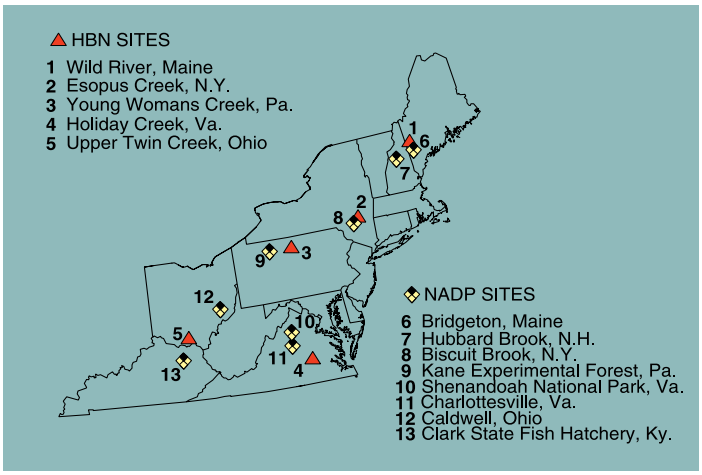


Figure 3. Locations of selected National Atmospheric Deposition Program (NADP) and Hydrologic Benchmark Network (HBN) sites in the northeastern United States.

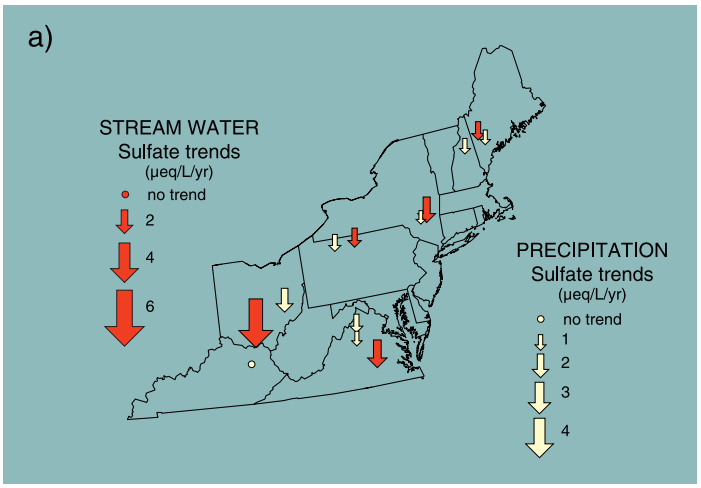
ecosystem acidification models predict that surface waters would respond to reduced sulfuric acid deposition with higher pH and alkalinity and lower SO_4 and base-cation concentrations (Galloway and others, 1983; Ruess and Johnson, 1986). However, stream-water data from Hubbard Brook, New Hampshire, indicate that, although SO_4 and base-cation concentrations have decreased, pH and alkalinity have not increased (Likens and others, 1996). It is uncertain whether the stream-water response at Hubbard Brook will occur in other streams in the region.

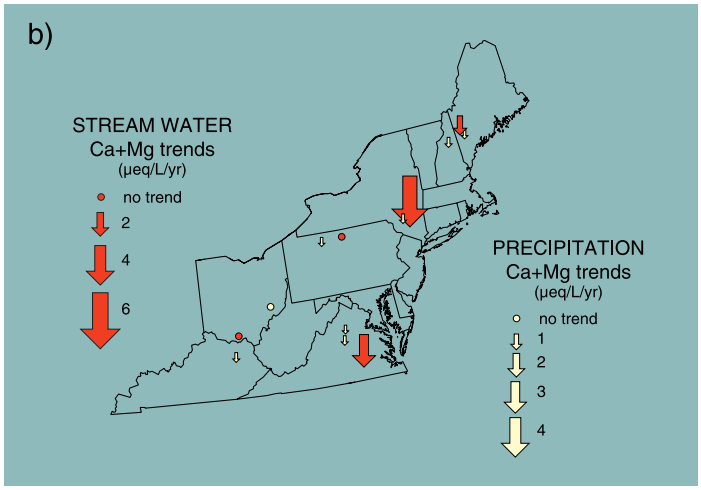
The U.S. Geological Survey (USGS) has monitored stream-water chemistry and discharge at a national network of small headwater basins since the mid-1960's through the Hydrologic Benchmark Network (HBN) program (figs. 2 and 3). Because the program is of national scope and the basins are relatively undisturbed, the HBN provides a unique opportunity for scientists to evaluate regional or national trends in stream-water quality that may be related to changes in atmospheric deposition. This fact sheet summarizes the results of a study in which precipitation data from eight precipitation monitoring sites and stream-water data from five HBN sites in the northeastern United States were analyzed for trends in concentrations of selected solutes from 1984 through 1996 (all results presented herein pertain to water years, which begin in October and end in September). The study focused on trends in SO_4, Ca + Mg, and acidity in precipitation and SO_4, Ca + Mg, and alkalinity in stream water. These chemical constituents probably are the main solutes controlling the long-term acid/base status of surface waters in the study basins. Several recent studies of small basins in the northeastern United States indicated that nitrogen compounds may be an increasingly important source of acidity to precipitation and stream water (Murdoch and Stoddard, 1992; Stoddard, 1994). However, stream-water nitrate concentrations at the HBN sites used in this study generally were near the analytical detection limit and indicated no significant trends. The low nitrate concentrations in the HBN streams probably are due to the relatively long flow paths and extensive soil development in the HBN basins. Because stream-water nitrate showed no significant trends, and precipitation nitrate showed only one weak trend, nitrogen compounds are not discussed further in this fact sheet. Ca and Mg were considered together in the study because of their similar geochemical behavior and because they usually were the dominant cations in stream water. Additional information on the methods used and results of the study are presented in Clow and Mast (1999), along with additional analyses of data covering 1968 through 1983.

Site Descriptions

The precipitation monitoring sites used in this study are part of the USGS National Atmospheric Deposition Program (NADP) (fig. 3). The NADP was initiated in the late-1970's and is a national network designed for long-term monitoring of precipitation chemistry. Startup dates of the NADP sites used in this study range from 1978 to 1984, and all sites used in this study are currently in operation.

The HBN sites used in this study are headwater basins that drain mostly undeveloped forested areas (fig. 3) ranging in size from 22 to 180 square kilometers. Soils at all of the sites are well drained and acidic and have 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 SO_4 concentrations exceed or are nearly equivalent to alkalinity at all of the sites, except Holiday Creek, where atmospheric SO_4 seems 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 headwater streams near Esopus Creek has been documented during storms (Murdoch and Stoddard, 1993; Mast and Turk, 1999).





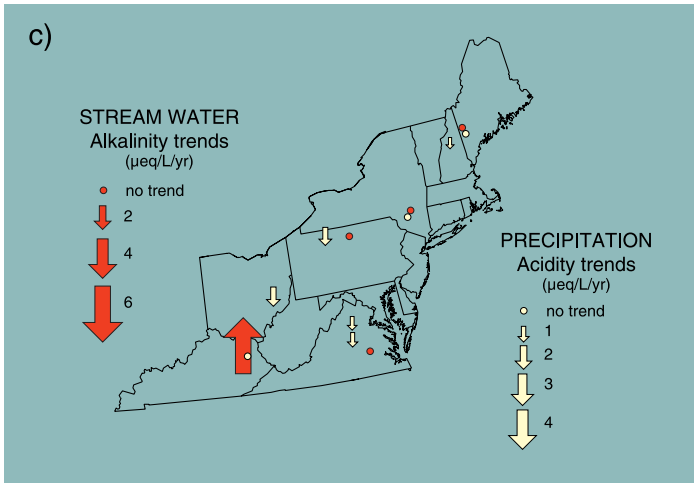


Figure 4. Trends in concentrations of (a) sulfate, (b) calcium plus magnesium, and (c) acidity and alkalinity in precipitation and stream water at selected National Atmospheric Deposition Program and Hydrologic Benchmark Network sites in the northeastern United States. Size of arrow is proportional to magnitude of trend ($p \leq 0.1$).

Methods of Statistical Analyses

Precipitation and stream-water data were tested for trends in concentrations using the seasonal Kendall test (SKT). The SKT is well suited for analyzing water-quality data because it can account for variations in chemistry that are related to seasonal patterns in solute concentrations or to changes in discharge or precipitation amount (Schertz and others, 1991). Prior to trend analyses, data were screened for outliers or possible periods of analytical bias. Suspect data were removed from the data set or adjusted using criteria and methods described in Clow and Mast (1999).

Trends in Precipitation and Stream-Water Chemistry

Concentrations of SO_4 decreased at seven of eight precipitation monitoring sites and in all of the streams during 1984–96 (fig. 4a). The decreases in precipitation SO_4 concentrations probably reflect decreased SO_2 emissions during the study period. The magnitudes of the decreases in precipitation SO_4 concentrations generally were similar to magnitudes of the trends in stream-water SO_4 concentrations, indicating that changes in precipitation chemistry could account for the changes in stream-water chemistry. Changes in land use and analytical bias were evaluated as other possible causes for the decreases in stream-water SO_4 concentrations, but the analysis indicated that those causes were relatively unimportant in determining trends in stream-water SO_4 concentrations (Clow and Mast, 1999).

Concentrations of Ca + Mg decreased at seven of eight precipitation monitoring sites and in three of five streams during 1984–96 (fig. 4b). The decreases in precipitation Ca + Mg concentrations probably reflect decreased inputs of particulates, such as dust and soot, to the atmosphere. National particulate emissions are estimated to have decreased 17 percent between 1988 and 1995 (Fitz-Simons and others, 1996). The decreases in stream-water Ca + Mg concentrations probably are due to a combination of decreased Ca + Mg deposition and decreased leaching of Ca and Mg from the soil. Decreased leaching of Ca and Mg could be related to lower acidic deposition rates or might be occurring because Ca and Mg have been depleted from the soils (Likens and others, 1996). The distinction is important because nutrient-poor soils are less able to support healthy forests.

Precipitation acidity decreased at five of eight precipitation monitoring sites during 1984–96, but alkalinity increased in only one stream (fig. 4c). The magnitudes of the decreases in precipitation acidity generally were similar to magnitudes of the trends in precipitation SO_4 (fig. 4a), indicating that recent decreases in SO_4 deposition are now being reflected in decreased precipitation acidity. Changes in stream-water alkalinity reflect a balance between decreases in stream-water SO_4 and Ca + Mg. In streams where SO_4 and Ca + Mg decreased, alkalinity showed no trend; however, where SO_4 decreased and Ca + Mg was stable, alkalinity increased at one of two sites. The balance between SO_4, Ca + Mg, and alkalinity is due to the neutralizing effect of chemical reactions in soil

that involve Ca and Mg, such as cation exchange and mineral weathering. Those reactions generally neutralize acidity or generate alkalinity, which then may be transported to aquatic ecosystems by flowing soil water.

Implications of Results

The consistency of and similarity in direction and magnitude of precipitation and stream-water trends in SO_4 concentrations indicate that streams in the northeastern United States may be responding to regional changes in atmospheric deposition. Decreases in stream-water SO_4 concentrations are consistent with predictions made by conceptual ecosystem acidification models and with trends at intensively studied sites in the northeast, such as Hubbard Brook, New Hampshire. The decreases in Ca + Mg concentrations in some of the HBN streams also are consistent with trends at Hubbard Brook, where depletion of cations from the soil has been implicated (Likens and others, 1996).

Although decreases in SO_2 emissions are now apparently being reflected in decreased precipitation and stream-water SO_4 concentrations, the decreases have not yet resulted in 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 by weathering and atmospheric deposition. In areas where forests are aggrading, recovery of stream-water alkalinity will be further delayed due to the acidifying effect of biomass accumulation. 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.

References Cited

Clow, D.W., and 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, v. 35, no. 2, p. 541–554.

Driscoll, C.T., and Van Dreason, R., 1993, Seasonal and long-term temporal patterns in the chemistry of Adirondack lakes: Water, Air, and Soil Pollution, v. 67, p. 319–344.

Fitz-Simons, T., Freas, W., Guinnup, D., Hemby, J., Mintz, D., Sansevero, C., Schmidt, M., Thompson, R., Wayland, M., and Damberg, R., 1996, National air quality and emissions trends report, 1995: Research Triangle Park, N.C., Environmental Protection Agency Report EPA–454/R–96–005, 168 p.

Galloway, J.N., Norton, S.A., and Church, M.R., 1983, Freshwater acidification from atmospheric deposition of sulfuric acid—A conceptual model: Environmental Science and Technology, v. 17, no. 11, p. 541A–545A.

Gschwandtner, G., Wagner, J.K., and Husar, R.B., 1988, Comparison of historic SO_2 and NO_x emission data sets: Research Triangle Park, N.C., U.S. Environmental Protection Agency Report EPA–600/7–88–009a, 167 p.

Likens, G.E., and Bormann, F.H., 1995, Biogeochemistry of a forested ecosystem (2d ed.): New York, Springer-Verlag, 159 p.

Likens, G.E., Driscoll, C.T., and Buso, D.C., 1996, Long-term effects of acid rain—Response and recovery of a forest ecosystem: Science, v. 272, p. 244–246.

Long, R.P., Horsley, S.B., and Lilja, P.R., 1997, Impact of forest liming on growth and crown vigor of sugar maple and associated hardwoods: Canadian Journal of Forest Research, v. 27, p. 1560–1573.

Lynch, J.A., Bowersox, V.C., and Grimm, J.W., 1996, 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. Geological Survey Open-File Report 96–346, 100 p.

Mast, M.A., and Turk, J.T., 1999, Environmental characteristics and water quality of Hydrologic Benchmark Stations in the eastern United States, 1963–95: U.S. Geological Survey Circular 1173–A, 158 p.

Murdoch, P.S., and Stoddard, J.L., 1992, The role of nitrate in the acidification of streams in the Catskill Mountains of New York: Water Resources Research, v. 28, no. 10, p. 2707–2720.

_____1993, Chemical characteristics and temporal trends in eight streams of the Catskill Mountains, New York: Water, Air, and Soil Pollution, v. 67, p. 367–395.

Nizich, S.V., Pierce, T., and Hohenstein, W., 1995, National air pollutant trends, 1900–1994: Research Triangle Park, N.C., U.S. Environmental Protection Agency Report EPA–454/R–95–011, 219 p.

Ruess, J.O., and Johnson, D.W., 1986, Acid deposition and the acidification of soils and waters: New York, Springer-Verlag, 120 p.

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

Shortle, W.C., Smith, K.T., Minocha, R., Lawrence, G.B., and David, M.B., 1997, Acidic deposition, cation mobilization, and stress in healthy red spruce trees: Journal of Environmental Quality, v. 26, p. 871–876.

Stoddard, J.L., 1991, Trends in Catskill stream water quality—Evidence from historical data: Water Resources Research, v. 27, no. 11, p. 2855–2864.

_____1994, Long-term changes in watershed retention of nitrogen, *in* Baker, L.A., ed., Environmental chemistry of lakes and reservoirs: American Chemical Society, ACS Advances in Chemistry Series, p. 223–284.