Temporal Trends in the Acidity of Precipitation and Surface Waters of New York

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Temporal Trends in the Acidity of Precipitation and Surface Waters of New York

By Norman E. Peters, Roy A. Schroeder, *and* David E. Troutman

Abstract

Statistical analyses of precipitation data from a nine-station monitoring network indicate little change in pH from 1965–78 within New York State as a whole but suggest that pH of bulk precipitation has decreased in the western part of the State by approximately 0.2 pH units since 1965 and increased in the eastern part by a similar amount. This trend is equivalent to an annual change in hydrogen-ion concentration of 0.2 microequivalents per liter.

An average annual increase in precipitation quantity of 2 to 3 percent since 1965 has resulted in an increased acid load in the western and central parts of the State.

During 1965–78, sulfate concentration in precipitation decreased an average of 1–4 percent annually. In general, no trend in nitrate was detected. Calculated trends in hydrogen-ion concentration do not correlate with measured trends of sulfate and nitrate, which suggests variable neutralization of hydrogen ion, possibly by particles from dry deposition. Neutralization has produced an increase of about 0.3 pH units in nonurban areas and 0.7 pH units in urban areas.

Statistical analyses of chemical data from several streams throughout New York suggest that sulfate concentrations decreased an average of 1 to 4 percent per year. This decrease is comparable to the sulfate decrease in precipitation during the same period. In most areas of the State, chemical contributions from urbanization and farming, as well as the neutralizing effect of carbonate soils, conceal whatever effects acid precipitation may have on pH of streams.

INTRODUCTION

During the last 30 to 50 years, a significant decrease in pH of atmospheric precipitation[1] has been noted in Europe (Barrett and Brodin, 1955; Oden, 1976; Wright and Gjessing, 1976) and in much of North America (Gambell and Fisher, 1966; Cogbill and Likens, 1974; Cogbill, 1976; Dillon and others, 1978). Acid atmospheric precipitation has been defined as rain or snow having a pH less than 5.6 (Barrett and Brodin, 1955; Likens, 1976), the value of pure water in equilibrium with ambient levels of atmospheric carbon dioxide. During the late 1970's, the average pH of precipitation calculated from the average hydrogen-ion concentration in much of the Northeastern United States ranged from 4.0 to 4.2 annually (Likens, 1976). The decrease in the pH of precipitation from a background of 5.6 to 4.0 is equivalent to a 40-fold increase in hydrogen ion concentration. Because long-term, continuous records of precipitation quality are not available, it is difficult to determine precisely the time of onset of acid precipitation in New York, although it is believed to have been between 1930 and 1950 (Cogbill and Likens, 1974). Similarly, the paucity of precipitation-quality records prior to 1964, when the first monitoring stations were installed, makes delineation of historical trends difficult.

In the absence of complete long-term precipitation-quality records, previous studies of trends in precipitation chemistry were either based on short periods of record (Pearson and Fisher, 1971; Likens, 1972; Tabatabai and Laflem, 1976; Richardson and Merva, 1976), were done at only one or two sites (Jacobson and others, 1976; Liljestrand and Morgan, 1978; Lewis and Grant, 1980), or were based on discontinuous records (Cogbill and Likens, 1974). Since 1965, the U.S. Geological Survey has operated a network of nine precipitation-quality monitoring stations in New York State; these provide some of the longest continuous records of precipitation quality in the United States.

Purpose and Scope

The purpose of this report is to analyze 13 years of data (1965–78) from the nine collection sites in New York to assess trends in precipitation acidity and to determine to what extent these trends are local or regional. A trend analysis of selected streams having continuous long-term water-quality records and representing a variety of land uses is included to evaluate effects of acid precipitation on surface-water quality.

Acknowledgments

Thanks are extended to the many observers who collected the data and maintained the sampling equipment. Data on rainfall quantity at each site were provided by the National Weather Service; financial support was provided by the New York State Department of Environmental Conservation and the New York State Energy Research and Development Authority.

SOURCES AND EFFECTS OF ACID PRECIPITATION

Sulfuric acid, nitric acid, and, to a much lesser extent, hydrochloric acid are the predominant strong mineral acids that contribute to the acidity of precipitation (Likens and Bormann, 1974; Galloway and others,

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[1] The term "precipitation" in this report refers to atmospheric, not chemical, precipitation.

1976). These acids are formed when sulfur and nitrogen oxides oxidize and (or) hydrolyze in the presence of water.

Natural sources of sulfate in the atmosphere include aerosols from sea spray, volcanic emissions, and readily oxidized hydrogen sulfide released from the anaerobic decomposition of organic matter in swamps and bogs (Robinson and Robbins, 1970a). Natural sources of nitrogen include nitrogen oxides produced by micro-organisms in soils and, to a lesser extent, the fixation of nitrogen as oxides by lightning (Robinson and Robbins, 1970b). Large increases in the free-acid concentration[2] (decrease in pH) of precipitation result from emissions of sulfur and nitrogen oxide gases to the atmosphere from the combustion of fossil fuels (Likens, 1976; Shinn and Lynn, 1979). Galvin and others (1978) and Samson (1978), tracing storm trajectories, attributed high sulfur dioxide concentrations to sources south and west of New York, and implied that these high concentrations are derived from air masses that stagnate over the heavily industrialized areas of the Ohio River valley and eventually advect into New York and the Northeast.

In Europe, where precipitation data have been collected by the European Atmospheric Chemistry Network and International Meteorological Institute since 1940 (Eriksson, 1960), increases in the hydrogen-ion (free-acid) concentration of precipitation seem to have been associated with increases in atmospheric sulfate concentrations (Oden, 1976; Granat, 1978). In contrast, data collected in central New York and at Hubbard Brook Experimental Forest in New Hampshire indicate that sulfate concentration has decreased by as much as 70 percent since 1950, yet sulfate is still the predominant anion in precipitation in most of the Northeast, and that much of the concentration decrease occurred between 1950 and 1955 (Likens and Bormann, 1974; Likens and others, 1976). However, the concentration of nitrate in precipitation has increased in the Northeast, particularly since the early 1960's (Likens and Bormann, 1974; Cogbill and Likens, 1974).

The low pH of precipitation in North America is most pronounced in the Northeast, including New York State. Likens and Bormann (1974) reported an annual mean pH of 4.03 in wetfall at Hubbard Brook Experimental Forest in New Hampshire for 1970-71 (pH of wetfall in central New York during the same period ranged locally from 3.91 to 4.02). In addition, Miller and others (1978), from a trajectory analysis of storms in Central New York, associated sources of high sulfur southwest of this area with acid precipitation.

Decreases in pH of surface water as a result of acid precipitation are most pronounced in terrain lacking carbonate rock, which neutralizes excess hydrogen concentration more rapidly than do other rock types. Thus, areas containing crystalline or metasedimentary bedrock and lacking carbonate rock have been identified as sensitive to acid precipitation (Hendrey and others, 1980). The Adirondack Mountain region of northeast New York is such an area. In a synoptic survey of lakes in the Adirondacks, Schofield (1976) found that 50 percent of the lakes at high elevation (above 600 m) had a pH less than 5.0 and that 90 percent of these no longer contained fish. A similar survey of many of these lakes from data collected during 1929–37 revealed that only 4 percent had pH values less than 5.0 or were devoid of fish. Recent synoptic studies of lakes in Scandinavia have revealed similar trends (Wright and Gjessing, 1976).

Although nearly all streams undergo some degree of neutralization through interaction with the soils and bedrock, the smaller headwater streams are buffered mainly by aluminum hydroxides rather than by carbonates, a condition that results in less neutralization (Johnson, N. M., 1979). In the Adirondack Mountains of New York, where appreciable quantities of acid precipitation are stored in the winter snowpack, many streams and lakes, even in well-buffered areas, experience a sharp temporary decrease in pH during the spring snowmelt, when large quantities of concentrated acid accumulated during the winter are released from the snowpack and transported by meltwater (Galloway and others, 1980). This phenomenon was also observed in Norway (Johannessen and Henriksen, 1978).

Even though delineation of trends in pH has been hindered by a lack of continuous or long-term records and by seasonal fluctuations that are difficult to differentiate during analysis of the data, studies by C. L. Schofield (Cornell Univ., Department of Natural Resources, written commun., 1975) on two Adirondack streams and by A. H. Johnson (1979) on two headwater streams in the New Jersey Pine Barrens indicate trends of decreasing pH; data from Hinckley Reservoir in the Adirondack Mountains reveal a similar decrease (C. L. Schofield, written commun., 1975). Even on Long Island, N.Y., precipitation is reported to have a significant influence, as indicated by a recent decline in pH of water from the major confined (Magothy) aquifer (Pearson and Fisher, 1971).

Although the disappearance of fish from lakes is the most dramatic example of adverse effects of acid precipitation (Schofield, 1976, 1977), other harmful effects have been suggested, including increased chemical weathering of manmade structures and possibly

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[2] The activity of hydrogen ion is equal to 10^{-pH}. In dilute solutions such as atmospheric precipitation, activity is nearly equal to concentration. Hence, hydrogen-ion (also called free-acid) concentration is calculated in this study from the measured pH and is assumed to be equal to the activity.

deleterious effects on human beings (Likens, 1976, and references therein). In addition, toxic levels of lead and copper have been found in tap water from several communities using surface-water supplies in unbuffered areas of New York (Turk and Peters, 1977); the elevated concentrations are attributed to increased dissolution of heavy metals from the pipes and soldered joints of the distribution system.

The effect of acid precipitation on biological systems is largely unknown, and study results appears somewhat contradictory. Some studies suggest that forest productivity is reduced and agricultural yields are decreased (Likens, 1976, and references therein), while others indicate certain beneficial effects. For example, the increased concentrations of sulfate and nitrate in acid precipitation may provide an important source of plant nutrients to deficient ecosystems (Barica and Armstrong, 1971; Schindler and others, 1976) and could possibly increase crop yields (Maugh, 1979).

METHODS

Network Design

Precipitation

The precipitation-quality monitoring network in New York State, operated by the U.S. Geological Survey in cooperation with the New York State Department of Environmental Conservation, was designed to provide data and continuous records on atmospheric contributions for use in hydrologic and geochemical studies. The network consists of nine sampling stations; eight are within New York, the other is in Pennsylvania near the New York State border (fig. 1). Details on the selection of sites are described by Pearson and Fisher (1971). In this study, bulk collectors (Whitehead and Feth, 1964) were established to obtain a monthly composite sample of wet plus dry fallout. The precipitation network contains two coastal stations, two urban stations (one of which is also coastal), and six rural inland stations.

Surface Water

The surface-water stations used in this study are distributed uniformly across the State (except on Long Island) and were selected to represent a variety of land uses. All stations had complete records of discharge and water quality for the period to be analyzed.

Location of the precipitation and surface-water sites, and also the predominant bedrock type underlying each site, is shown in figure 1. Additional information about the precipitation sites is given in table 1; information on surface-water sites is given in table 2.

Sampling Techniques

Precipitation

The type of precipitation collector used in 1965 (fig. 2A) consisted of a glass collection funnel with a fritted glass disk at the base. Water entering the funnel discharged through Tygon[3] tubing into a polyethylene collection bucket. The unit was thermostatically con-

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[3] Use of brand names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

Table 1.—Period of record and predominant land use at precipitation-monitoring sites
[Site locations are given in fig. 1]

Site	Latitude (North)	Longitude (West)	Period of record	Predominant land use	Remarks
Coastal					
Mineola	40°44′17″	73°38′17″	Nov. 1965–Aug. 1976	Urban	Located on office rooftop.
Upton	40°52′16″	72°53′20″	Aug. 1965–Aug. 1973 Mar. 1975–Sept. 1979	Residential	Refrigerated old-style sampler.
Urban					
Albany	42°44′35″	73°48′30″	Aug. 1965–Sept. 1978	Urban	Located at Albany airport.
Rural inland					
Rock Hill	41°37′25″	74°31′17″	Aug. 1965–Sept. 1978	Residential, woodlands	Located in back yard.
Athens, Pa	41°55′31″	76°31′35″	do	Agricultural	Located on large dairy farm and near fuel pump.
Salmanca	42°06′00″	78°45′00″	do	Woodlands	Located at Allegany State Park visitor center.
Mays Point	42°59′55″	76°45′45″	do	Agricultural, wetlands	Located on Erie Barge Canal.
Hinckley	43°18′35″	75°06′35″	do	Woodlands	Located near reservoir.
Canton	44°34′40″	75°06′40″	do	Agricultural	Located on agricultural extension station.

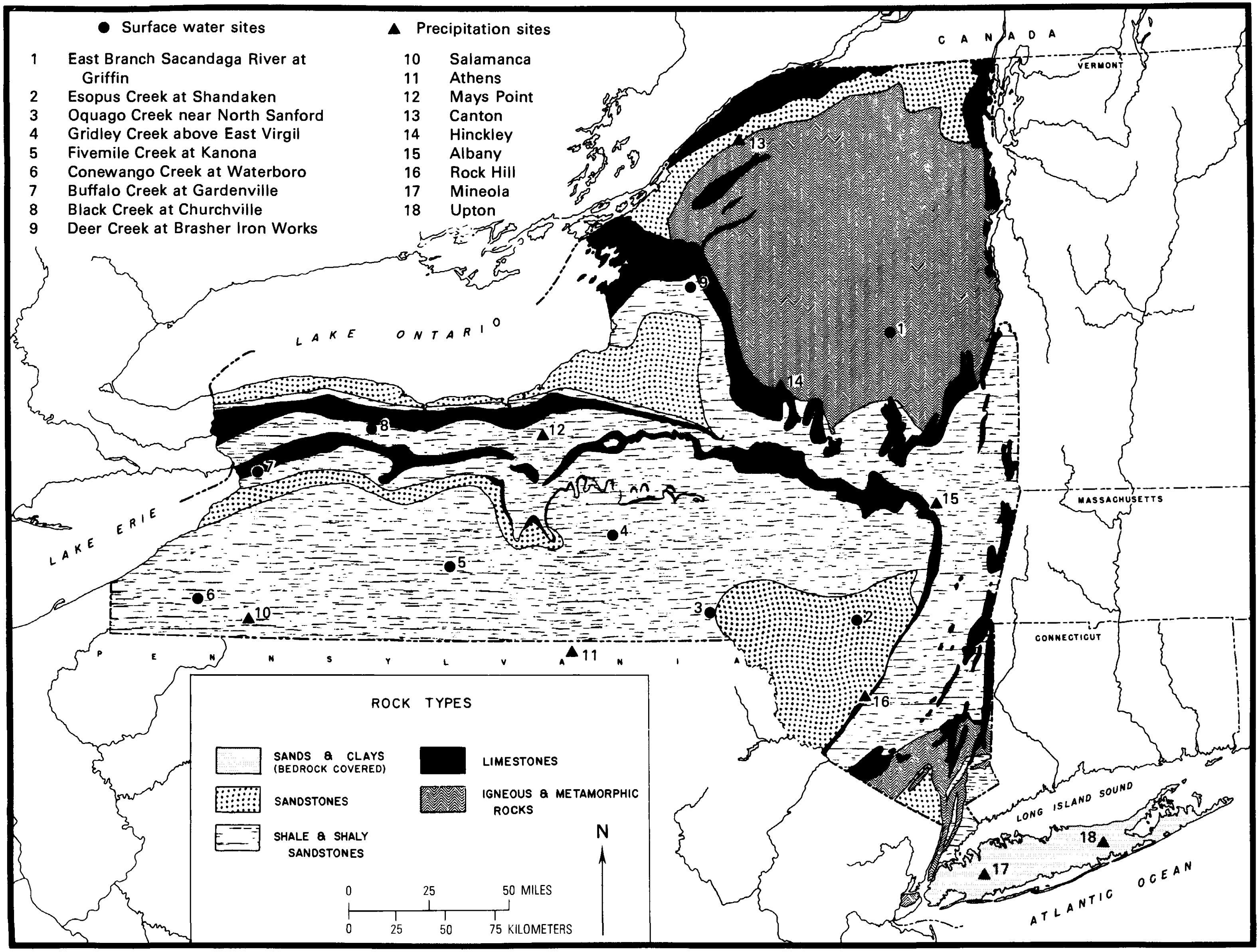

Figure 1.—Location of precipitation and surface-water-measurement sites and associated bedrock geology (modified from Thompson, 1966, p. 24; reproduced with permission of publisher).

Table 2.—Period of record and basin characteristics of surface-water measurement sites
[Locations are given in fig. 1]

Station name	USGS station No	Drainage area (km ^{2})	Period of record	Land use,[1] in percent				Remarks
				Agricultural	Woodlands	Urban	Residential	
East Branch Sacandaga River at Griffin.	01319000	295	Aug. 1965–May 1975	<1	99	<1	<1	
Esopus Creek at Shandaken.	01362198	154	Aug. 1963–Sept. 1979	<1	97	<1	2	USGS benchmark station; some months missing from record.
Oquaga Creek near North Sanford.	01425675	12.2	Mar. 1971–Aug. 1979	14	85	<1	<1	Some months missing from record.
Gridley Creek above East Virgil.	01509150	26.9	Dec. 1974–Sept. 1979	47	52	<1	<1	
Fivemile Creek near Kanona.	01528000	173	Mar. 1966–May 1975	39	60	<1	<1	
Conewango Creek at Waterboro.	0301300	757	Oct. 1965–Oct. 1975	48	51	<1	<1	
Buffalo Creek at Gardenville.	04214500	373	July 1966–May 1975	47	46	3	4	
Black Creek at Churchville.	04231000	319	Aug. 1965–May 1975	72	25	<1	2	Slight regulation due to pumping.
Deer River at Brasher Iron Works.	04269500	490	________do________	30	69	<1	<1	

[1] Land-use data were obtained by digitizing the associated land-use categories for the stream basins from 1968 Land Use and Natural Resources Inventory (LUNR) map overlays.

trolled to maintain a temperature above 4°C so that snow entering the funnel would melt. The fritted glass disk was replaced each month. Some collectors contained a plug of spun glass above the fritted glass disk to reduce clogging of the disk. Additional details of the design are described by Gambell and Fisher (1966).

Beginning in 1977, a new type of collector (fig. 2*B*) became available and gradually replaced the old ones. The newer collectors use a polyethylene funnel that discharges through silastic tubing into a teflon collection bottle. A loop in the silastic tubing provides a vapor lock to retard evaporation. The sampler is thermostatically controlled for snow collection, as are the older-style collectors. The only site at which an old-style collector remained in use as of 1980 was at Upton, on Long Island (fig. 1).

Surface Water

Water-quality and water-discharge data used in the surface-water trend analyses were collected by the U.S. Geological Survey at gaged sites. (Site locations are shown in fig. 1.) Samples for water-quality analysis were collected at least monthly by methods described by Brown and others (1970); discharge at the time of sample collection was measured by standard procedures for stream gaging (Carter and Davidian, 1968).

Analytical Techniques

Data used in this report include concentrations of sodium, potassium, calcium, magnesium, pH, ammonium, nitrate (plus nitrite), chloride, sulfate, bicarbonate (or alkalinity)[4], and specific conductance. (These data are published in U.S. Geological Survey, 1964-75; 1976-80.) Precipitation-quantity data were obtained from records of National Weather Service gages at or near the network sites (U.S. National Oceanographic and Atmospheric Administration, 1965-78). Surface-water analyses were, in general, done on monthly grab samples filtered through a 0.45-μm (micrometer) membrane filter. Monthly bulk precipitation samples were decanted but not filtered.

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[4] Bicarbonate concentration of precipitation is not included in this report because samples were analyzed for bicarbonate only on a sporadic basis.

Figure 2.—Apparatus used to collect bulk precipitation samples. A, Collector used from 1965–77. B, Collector used since 1977.

All conductance and pH measurements were made by the U.S. Geological Survey in Albany, N.Y. Before 1977, analyses for the other chemical constituents were made in the Albany laboratory; thereafter they were made in the Survey's National Water Quality Laboratory in Atlanta, Ga. Methods used for chemical analysis are described by Skougstad and others (1979). Although analytical procedures have been modified during recent years through technical advances, it is beyond the scope of this report to discuss these changes in detail.

Because chemical concentrations are typically much lower in precipitation than in surface water, measured chemical concentrations of precipitation samples may be less precise than those of surface water. Also, detection limits were lower in the later part of this study, which suggests that the recent concentration data may be more accurate than the earlier values. However, precision and accuracy of pH and conductance measurements have not changed since 1965.

Data Editing

Precipitation

The data used in this study were modified to provide single monthly values (where possible) for trend analysis. Precipitation samples were designated by month of collection. Because the period of sample collection did not always coincide with the calendar month, each sample was designated by the month containing the greatest number of collection days. In the few instances (less than 5 percent) when precipitation quantity was not available from the nearby Weather Service gage, quantity was estimated from the nearest adjacent gage, typically within 20 miles of the collector.

Stream Discharge

Daily mean discharge values were used in less than 2 percent of the cases; otherwise instantaneous discharges were used. When multiple monthly chemical data were collected, only the first observation was used in trend analysis. In the few instances in which data from a specific month were unavailable, data from the previous or following month were used. This constituted fewer than 2 percent of the observations at any given station.

Nitrogen in Precipitation and Surface Water

The precipitation samples analyzed for nitrogen species in this study varied in chemical state and physical phase. To obtain a continuous record of sufficient length, the results were combined into a single data set represented as nitrate. Accordingly, nitrite values, when available, were included with nitrate. The error introduced by this procedure was negligible because nitrite seldom constitutes more than 5 percent of nitrate concentration. In addition, results for dissolved and total species are assumed to be interchangeable. The extremely high solubility of nitrate insures that dissolved and total concentrations should be equal.

Surface-water data used in this study included only the nitrate, nitrite, and ammonium values obtained after July 1971.

Conductance and Electroneutrality of Precipitation and Surface Water

The initial step in screening the data was to identify outlying values and then to review available field and laboratory notes and correct transcription errors. The next step was to remove anomalously low pH values (pH is generally difficult to measure accurately in solutions of low ionic strength, such as precipitation). To determine the lowest acceptable pH value, a maximum permissible hydrogen-ion concentration (representing minimum pH value) was calculated.[5] Because specific conductance, in micromhos per centimeter (μmho/cm), of hydrogen ion in dilute solution is about 380 times its concentration, in milliequivalents per liter (meq/L),[6] the maximum permissible concentration of hydrogen ion was obtained by dividing measured specific conductance by 380. If the measured concentration exceeded the calculated value by more than 25 percent,[7] the value was deleted from the data set. This procedure eliminated about 5 percent of the pH measurements.

The final step, deletion of anomalous chemical concentrations, was based on the requirement of electroneutrality that cation equivalents must equal anion equivalents. If the difference between cation and anion equivalents in a sample exceeded the total ion equivalents by 25 percent or more, all results for that sample other than pH and conductance were deleted from the data set. In calculations for surface-water samples, cations considered were sodium, potassium, calcium, and magnesium; anions considered were bicarbonate, chloride, sulfate, and nitrate. In calculations for precipitation samples, cations were sodium, potassium, calcium, magnesium, ammonium, and hydrogen; anions were chloride, sulfate, and nitrate. If data on the concentration of any of these above constituents were unavailable, the test was not applied. All data-editing procedures were intended to minimize the potential for major errors.

Statistical Techniques

Regression Analysis

Least-squares regression analysis was used to determine the straight line best representing the set of points on a plot of concentration of a selected constituent against time. The slope of this line was taken as a measure of linear trend. Regressions were also used to determine the relationship between chemical concentration and stream discharge (or some function of discharge) and between chemical concentration of precipitation samples and precipitation quantity (or some function of quantity).

Precipitation Analysis

Chemical constituents of a bulk precipitation sample are derived from wetfall, dryfall, and gaseous transfer; chemical concentrations of a sample during a rainfall vary with quantity and duration of the event (Kennedy and others, 1979). The initial washout of ions from the atmosphere during a storm tends to concentrate chemical constituents in the sample, but these become diluted as the storm continues. It was anticipated that chemical concentration of monthly bulk samples might vary disproportionately with precipitation quantity, as expressed in equation 2; the logical

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[5] This procedure was based on the premise that no other constituents were contributing to measured specific conductance. In fact, other cations and anions would raise the conductance and in turn raise the calculated maximum permissible hydrogen-ion concentration. The degree of error resulting from this assumption is variable but on the order of 10-15 percent at low pH.

[6] At infinite dilution and 25° C, the equivalent conductances (in micromhos per centimeter per equivalent) of the following ions are hydrogen, 350; sulfate, 79; nitrate, 71. These equivalent conductances decrease with an increase in ionic strength of a solution.

[7] Because the contribution of other ions was ignored, the actual constraint is closer to 35-40 percent, which is equivalent to deleting values that were in error by more than 0.2 pH units.

alternative would be a direct relationship, as expressed in equation 1.

$$\text{Linear relationship: } C_i = aQ + b, \quad (1)$$

$$\text{Hyperbolic relationship: } C_i = (a/Q) + b, \quad (2)$$

where

C_i is the concentration,
Q is the precipitation quantity,
a is the slope of regression line, and
b is the intercept value.

If neither the hyperbolic nor the linear equation produces results that are significant to at least the 90-percent confidence level, or level of significance $\alpha < 0.1$, the null hypothesis that concentration is independent of quantity is not rejected, and predicted concentration is set equal to the mean concentration (equivalent to eq 1 with a slope of zero) for subsequent use in a nonparametric statistical test for temporal trends.

Surface-water Analysis

A general hyperbolic equation formulated by Johnson and others (1969) provided a more rigorous theoretical basis than did equations 1 or 2 for the mixing of a two-component system (ground-water and surface-water contributions):

$$\text{General hyperbolic relationship: } C_i = [1/(1 + \beta \cdot Q)]a + b, \quad (3)$$

where

β is a constant, described in the section Relationship Between Chemical Composition and Discharge, and
Q is stream discharge.

Equation 3 was used in this study for analysis of surface-water data with β values increasing from $10^{-5.5}$ to $10^{-2.0}$ $\text{km}^2 \cdot \text{d/m}^3$ in increments of $10^{0.5}$ (a total of eight possibilities).

Statistical Considerations

Residual values, which are the difference between predicted and measured concentrations from the best equation, as determined by the maximum R^2 (square of correlation coefficient), were selected for application in the nonparametric seasonal Kendall statistical test described below. R^2 is the proportion of the total variance in concentration explained by the regression model. (In tables throughout this report, R^2 is multiplied by 100 to express it as a percentage.)

The level of significance of linear regression relationships is established by computing the t-test statistic for the correlation coefficient (r) from a normally distributed population whose correlation coefficient is zero on the assumption that both the distributions of C_i are normal for each Q, and the variances for these distributions are constant for each Q. The significance of r is related to the number of observations. Hence, for a given level of significance, the required r value decreases as the number of observations increases. Furthermore, if temporal dependence exists among the data, the number of observations on which the significance of the relationships was based will be fewer than those used, and will result in nonsignificance for some relationships that are claimed to be significant. A more detailed discussion of levels of significance and related statistical concepts is given in Dixon and Massey (1969).

Nonparametric Seasonal Kendall Test

The seasonal Kendall test (Hirsch and others, 1982) is used to test whether the residuals from the regression of C_i on $f(Q)$ show a significant time trend. This type of test uses only the relative ranking of data and is advantageous in analyses of water-quality data that reflect seasonal variations or point-source loadings.

The seasonal Kendall test was used to compare residual values obtained from equations 1-3 for a given month with those of the same month of the most recent succeeding year for which data were available. If the comparison was positive (the succeeding value was higher), a value of +1 was recorded; if negative, a value of −1 was recorded. Summing all positive values and dividing by the number of entries yielded the test statistic, a fraction representing the temporal trend. This value (Kendall's τ) was then compared to the standard normal distribution function to establish the level of statistical significance. Using an average of the actual values rather than +1 or −1 gave the slope of the trend.

RESULTS AND DISCUSSION

Precipitation

Chemical Composition of Samples

As stated previously, the pH of precipitation in bulk collectors is a net result of chemical and biological interactions among materials contributed in wetfall and dryfall and through gaseous exchange. Materials are contributed from both manmade and natural sources, including sea spray, aerosols, dust, and ions dissolved in wetfall.

pH

According to a precipitation model proposed by Granat (1972), a simple stoichiometric relationship among major ions can be used to predict hydrogen-ion concentration. Because the ions derived from sea-salt particles (mostly sodium and chloride and some magnesium and sulfate) are already neutralized, hydrogen ions are the difference between the remaining acid-forming and base-neutralizing ions. The acid-forming anions (sulfate and nitrate) are partly neutralized by "excess" cations (those not included in the sea-salt component); hence, hydrogen-ion concentration can be calculated as the excess of anion over cation (excluding hydrogen) equivalents (electroneutrality). Despite complicating factors, such as anomalous materials introduced by dryfall, the 1-month storage period at ambient field conditions, and changes in collection and analytical methods over the years, results of this calculation show reasonably close agreement between calculated and measured hydrogen-ion concentrations (table 3). The largest difference, 25 μeq/L (microequivalents per liter), was in samples from Salamanca, in southwestern New York (fig. 1).

Mean chemical composition of precipitation in the nine-station precipitation network is given in table 3. For comparison, the volume-weighted mean composition of precipitation at three locations in central New York, as reported by Cogbill and Likens (1974), is included. Cogbill and Likens' data were based on storm-by-storm sampling between September 1972 and August 1973, about the midpoint of the Geological Survey's collection period. Data in table 3 indicate that pH in the Survey's network, excluding urban sites, was 0.2 to 0.3 pH units higher than that in Cogbill and Likens' study. This difference corresponds to a nearly 50-percent lower hydrogen-ion concentration in the Survey's records, which is 30 to 40 μeq/L less than in Cogbill and Likens' record. The lower hydrogen-ion activity in the Survey's data may be due to neutralization by dryfall in the bulk sample. Alkaline-earth elements (calcium and magnesium) are the predominant cations, followed at most stations by sodium, ammonium, and potassium.

Ion Concentration

Despite substantial differences between collection methods of the Geological Survey and of Cogbill and Likens (1974), the chemical composition of samples was surprisingly similar; the few large differences may generally be attributed to local influences. Major chemical characteristics of precipitation samples are described in the following paragraphs.

Ratio of sulfate to nitrate at the Geological Survey stations was about 3:1, and at Cogbill and Likens' central New York stations, about 2:1. However, the analytical technique for nitrate at the Geological Survey changed in spring 1969. A comparison of mean nitrate values for the time preceding this date with values thereafter indicates that the more recent values are about four times larger than the earlier ones (table 3). The ratio of sulfate to nitrate in the more recent data is 2.5:1, lower than that for the complete record but greater than the 2:1 ratio recorded by Cogbill and Likens (1974). No reason for this difference is apparent, although the higher ratio in the Survey's data reflects a combination of slightly higher sulfate along with lower nitrate concentrations.

Chloride concentrations varied widely from place to place; the lowest recorded values were at inland stations, such as Hinckley and Canton, and were about the same as at Cogbill and Likens' stations, which were also inland. Chloride concentrations at Mineola and Upton, near the coast, were markedly higher than at inland sites as a result of proximity to the ocean. The elevated concentrations of sodium and chloride at Albany may indicate contributions from local sources, perhaps road salt.

The high concentrations of magnesium in the coastal samples are attributed to marine sources, especially at Upton, which is less urbanized than Mineola. Subtracting the sea-salt contribution at Upton (on the assumption that the ratio of other ions to chloride in samples is identical to that in sea water and that chloride is entirely marine derived) reduces the mean calcium concentration from 0.024 to 0.022 meq/L, magnesium from 0.016 to 0.006 meq/L, sodium from 0.050 to 0.005 meq/L, and sulfate from 0.074 to 0.069 meq/L. The concentrations after subtraction of sea salt are comparable to inland concentrations.

Although Mineola and Upton are at similar distances from the ocean, Upton is less urbanized, and its collector is of the older type, in which a fritted glass filter is installed beneath the collection funnel and the sample is refrigerated. Ammonium and nitrate concentrations at Upton were lower than at other sites, which may have been a consequence of reduced biological activity in the refrigerated collector.

The impact of urbanization on bulk precipitation chemistry is seen in samples from both Mineola and Albany. The net effect at Albany was a reduction in hydrogen-ion concentration to one-fourth that at Cogbill and Likens' (1974) central New York sites and half that of the nonurban Geological Survey sites—an increase of several tenths of a pH unit. The major element contributing to neutralization at Albany was calcium, as indicated by its extremely high concentration in relation to the other cations. Apparently, the elevated levels of particulate material in an urban atmosphere were sufficient to neutralize precipitation in the bulk collector. However, it is not possible at present to determine how much of the neutralization took place in the collector and how much in the atmosphere beforehand.

Ammonium concentration in precipitation at the Athens, Pa., station was three times greater than at other sites. A principal source may have been decom-

Table 3.—Composition of precipitation samples from monitoring sites

[Chemical concentrations are given in milliequivalents per liter. Number of observations used in calculation of mean and standard deviation is in parentheses. Locations are given in fig. 1]

Constituent or characteristic	Monitoring site									Cogbill-Likens Study [1]
	Albany	Athens	Canton	Hinckley	Mays Point	Mineola	Rock Hill	Salamanca	Upton	
Precipitation quantity (cm/year)	103 ± 64 (147)	89 ± 50 (149)	94 ± 58 (138)	129 ± 52 (159)	91 ± 44 (155)	117 ± 61 (121)	123 ± 64 (144)	123 ± 58 (144)	123 ± 66 (146)	90 to 98
Hydrogen (measured)	.020 ± .028 (142)	.047 ± .041 (146)	.034 ± .027 (135)	.051 ± .036 (147)	.040 ± .032 (146)	.026 ± .030 (118)	.046 ± .039 (140)	.056 ± .052 (130)	.051 ± .034 (137)	.087
Hydrogen (calculated)	.017	.055	.027	.041	.038	.030	.053	.081	.050	.088
pH	4.69	4.32	4.46	4.29	4.39	4.58	4.33	4.25	4.29	4.06
Specific conductance (μmho/cm at 25° C)	36 ± 17 (147)	44 ± 22 (150)	34 ± 16 (141)	34 ± 13 (160)	38 ± 15 (156)	47 ± 35 (126)	36 ± 16 (146)	48 ± 40 (144)	38 ± 16 (146)	----
Total ions	.463 ± .252 (113)	.386 ± .234 (109)	.349 ± .227 (105)	.258 ± .095 (112)	.383 ± .214 (119)	.460 ± .237 (87)	.332 ± .228 (110)	.380 ± .279 (97)	.296 ± .108 (105)	.315
Calcium	.143 ± .095 (141)	.055 ± .058 (135)	.068 ± .065 (132)	.043 ± .035 (148)	.088 ± .060 (151)	.086 ± .071 (120)	.043 ± .040 (137)	.058 ± .085 (136)	.024 ± .019 (135)	.034
Magnesium	.021 ± .012 (141)	.014 ± .021 (136)	.025 ± .018 (132)	.012 ± .012 (148)	.022 ± .014 (151)	.045 ± .034 (120)	.018 ± .022 (138)	.015 ± .016 (136)	.016 ± .010 (135)	.008
Sodium	.031 ± .048 (141)	.021 ± .033 (136)	.019 ± .038 (132)	.010 ± .008 (148)	.023 ± .049 (151)	.058 ± .099 (120)	.016 ± .020 (138)	.030 ± .054 (137)	.050 ± .031 (134)	.005
Potassium	.006 ± .010 (141)	.007 ± .015 (136)	.007 ± .028 (132)	.003 ± .004 (148)	.005 ± .009 (151)	.004 ± .010 (120)	.020 ± .044 (138)	.008 ± .015 (137)	.003 ± .004 (134)	.002
Ammonium	.014 ± .019 (121)	.063 ± .066 (118)	.023 ± .023 (114)	.019 ± .021 (126)	.020 ± .026 (131)	.032 ± .032 (93)	.020 ± .035 (118)	.033 ± .069 (117)	.011 ± .012 (120)	.021
Sulfate	.131 ± .063 (139)	.130 ± .076 (137)	.104 ± .057 (131)	.084 ± .039 (148)	.110 ± .049 (151)	.128 ± .083 (122)	.098 ± .055 (138)	.140 ± .206 (138)	.074 ± .045 (137)	.098
Nitrate	.041 ± .029 (133)	.050 ± .062 (127)	.040 ± .035 (117)	.033 ± .025 (133)	.043 ± .030 (143)	.042 ± .035 (119)	.030 ± .025 (120)	.046 ± .062 (122)	.027 ± .017 (139)	.048
pre-1969	.037 ± 028 (38)	.009 ± 009 (27)	.015 ± 017 (32)	.012 ± .017 (24)	.015 ± .023 (33)	.015 ± .016 (37)	.009 ± .010 (23)	.015 ± .018 (26)	.011 ± .010 (38)	
post-1969	.043 ± .030 (95)	.056 ± .060 (100)	.049 ± .035 (85)	.033 ± .024 (109)	.051 ± .027 (110)	.054 ± .035 (82)	.035 ± .024 (97)	.054 ± .066 (96)	.033 ± .014 (101)	
Chloride	.036 ± .049 (140)	.026 ± .039 (136)	.017 ± .028 (131)	.012 ± .012 (148)	.013 ± .055 (151)	.065 ± .094 (121)	.027 ± .035 (137)	.025 ± 037 (138)	.054 ± .034 (137)	.012
Phosphate	.002 ± .003 (98)	.004 ± .006 (90)	.001 ± .002 (89)	.001 ± .002 (96)	.001 ± .002 (96)	.002 ± .003 (65)	.006 ± .011 (96)	.002 ± .003 (93)	.001 ± .001 (92)	----

[1] Data from Cogbill and Likens (1974).

posing animal wastes on the dairy farm where the collector is located. Although ammonia is a base, it did not cause a significant increase in pH, possibly because sulfate concentrations were high enough to neutralize most of the ammonia. In addition, oxidation of ammonium to nitrate during the month of field storage may have contributed some acid through the reaction

$$NH_4^+ + 2O_2 \rightleftharpoons NO_3^- + H_2O + 2H^+.$$

This hypothesis is supported by the observation that nitrate concentration was slightly higher at Athens than at other sites.

Potassium concentration at Rock Hill, in southeastern New York, was several times higher than at other stations. All other collectors in the network were either in open terrain or far enough from obstructions (such as trees) that the vertical angle between the collector's ground location and the top of the obstruction was less than 30°. At Rock Hill, the collector was among deciduous trees in a heavily wooded semiresidential area. Earlier studies, such as that of Madgwick and Ovington (1959), have shown that precipitation through a tree canopy becomes enriched with potassium, with a maximum enrichment in autumn and a minimum enrichment in spring. Potassium concentrations at Rock Hill in the late fall exceeded those in the early spring by more than an order of magnitude.

Interrelationship of Chemical Constituents

Linear regressions relating conductance and hydrogen concentration to concentration of selected constituents are given in table 4. Specific conductance of hydrogen ion exceeds that of other ions by a factor ranging from 5 to 8. The larger slopes (*a* values) in the conductance-against-total ions column (table 4) and in the conductance-against-hydrogen column represent stations at which the hydrogen ion is a major contributor to conductance. In general, these stations received less dryfall than the rest, as exemplified by the Albany station, an urban site having a large amount of dryfall and showing the lowest slope value in the conductance-against-hydrogen column.

In contrast to the conductance-against-total ions column, which indicates a statistically significant relationship at all stations, the acid-forming anions sulfate and nitrate showed a significant relationship at only four and seven stations, respectively. The only significant relationship between hydrogen and nitrate plus sulfate was at Hinckley and Upton. These stations had the lowest total ion concentrations, the smallest percent standard deviation in hydrogen concentration, and high hydrogen concentrations and are therefore the stations most likely to reflect changes in these acid-forming species. Furthermore, at all stations, the mean of the strong acid anion (sulfate plus nitrate) equivalents was at least twice the mean hydrogen-ion equivalents (table 3). The smallest difference between hydrogen and sulfate plus nitrate were at stations where the correlations were significant (Hinckley and Upton). Yet, this lack of stoichiometric balance illustrates the fact that hydrogen-ion concentration is a net result of a complex interaction among base-neutralizing cations as well as acid-forming anions. Also, as explained in the following section, ionic concentrations are themselves a function of precipitation quantity; therefore, any further statistical studies of these data should include a multivariate analysis to provide an understanding of the interrelationships of all species that potentially control the hydrogen-ion concentration.

Relationship of Chemical Concentration to Precipitation Quantity

Chemical concentration of bulk precipitation reflects contributions from both dryfall and wetfall. The proportion added in either form varies among constituents as well as among stations. If dryfall were the sole source of chemical constituents, wetfall would act as a diluent, and the concentration in bulk precipitation would decrease with increasing wetfall quantity. However, ions are also added in wetfall, so that dilution does not decrease concentration either as rapidly or as extensively as might be expected.

Both linear and hyperbolic regressions of major constituents were done to depict the relationship between chemical concentration and precipitation quantity and for use in the nonparametric time-trend analysis. Best least-squares relationships for each station are given in figures 3A–I. Where statistical significance at a level of 0.1 is not indicated, mean concentration is drawn as a horizontal line. However, even where a statistically significant relationship is not indicated, a functional relationship may still be possible.

The graphs in figure 3 indicate that predicted concentration generally decreases as precipitation quantity increases. An exception is hydrogen (fig. 4), which increases at all stations except Upton, although only two of these—Athens and Mays Point—show statistical significance ($\alpha < 0.1$). In all other respects, the combined data from all stations suggest a slight increase in hydrogen concentration as precipitation quantity increases.

As stated earlier, the concentration of hydrogen results from a complex interaction of many factors. Electroneutrality requires that if hydrogen concentration increases as precipitation quantity increases, the concentration of anions must decrease slightly less than those of the remaining cations (excluding hydrogen). Hence, visual inspection of the slope (rate of decrease) of the lines in figure 3 should indicate which ions affect

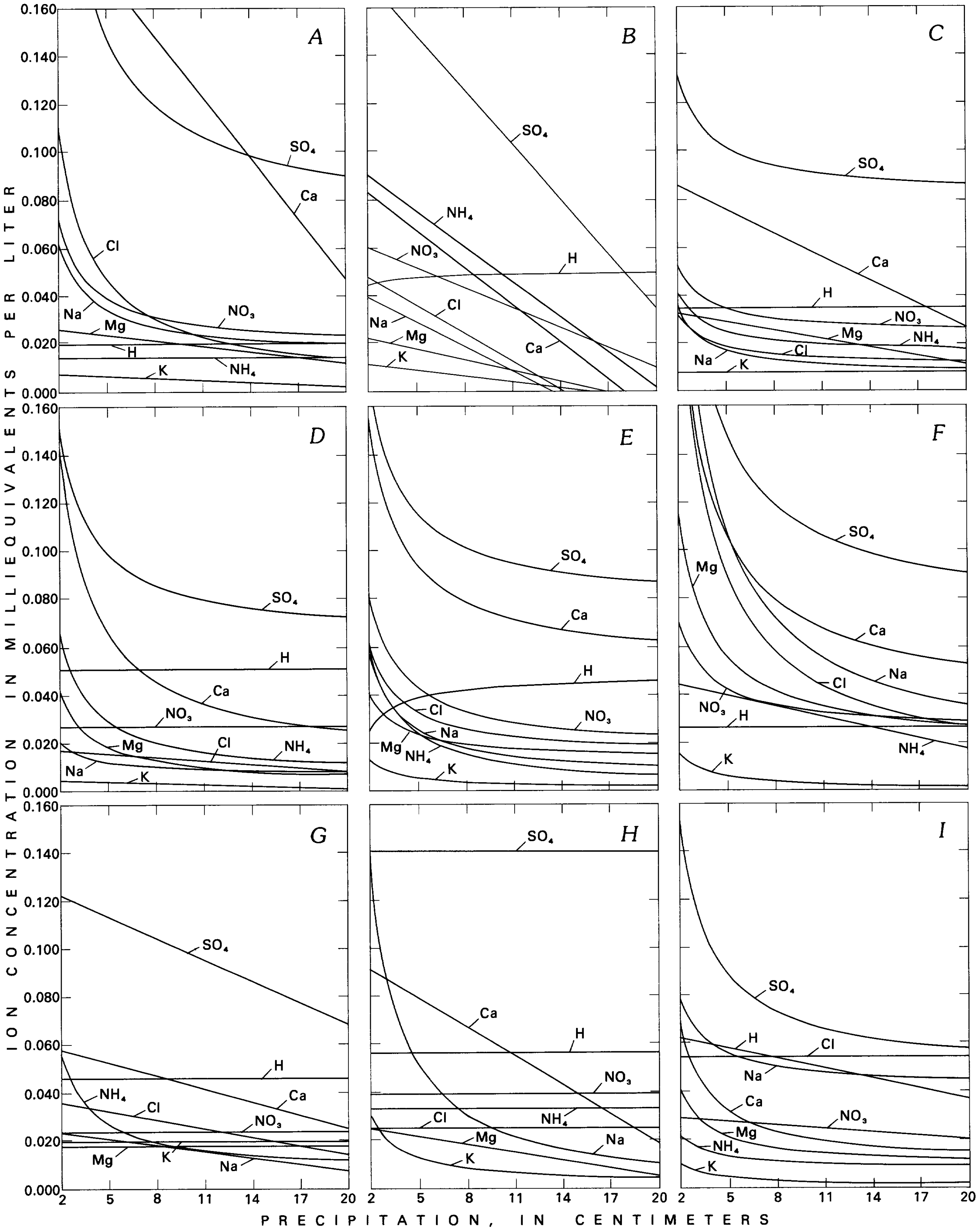

Figure 3.—Least-squares relationship between chemical concentrations and monthly precipitation quantity, 1965-78. Where no significant relationship exists at 0.1 level, mean concentration is shown as a horizontal line. *A*, Albany. *B*, Athens. *C*, Canton. *D*, Hinckley. *E*, Mays Point. *F*, Mineola. *G*, Rock Hill. *H*, Salamanca. *I*, Upton.

Table 4.—Linear regression relationships between selected chemical constituents of precipitation

[Equation is of the form $Y=aX+b$. Concentrations of total ions, hydrogen, nitrate, and sulfur are in milliequivalents per liter; specific conductance is in micromhos per centimeter at 25°C. Nitrate data are from spring 1969 through 1978. N is number of observations; R^2 is correlation coefficient. Locations are given in fig. 1]

	Specific Conductance (*Y*) vs Total ions (*X*)				Specific Conductance (*Y*) vs Hydrogen (*X*)				Hydrogen (*Y*) vs Nitrate (*X*)			
Station	*a*	*b*	*N*	100R^2	*a*	*b*	*N*	100R^2	*a*	*b*	*N*	100R^2
Albany	86.21	−3.48	114	[3]71.6	140.2	33.10	142	[3]5.1	0.1943	0.0139	89	[1]3.4
Athens	55.56	20.62	110	[3]47.4	228.3	32.69	145	[3]17.7	-----	-----	96	2.1
Canton	45.28	17.64	105	[3]52.7	191.88	28.18	135	[3]9.9	-----	-----	79	0.6
Hinckley	89.26	10.26	116	[3]49.8	256.97	20.83	147	[3]49.1	.3398	.0455	96	[2]4.2
Mays Point	51.06	18.96	118	[3]48.8	260.05	28.07	146	[3]30.0	-----	-----	100	.0
Mineola	49.61	16.65	93	[3]51.5	208.42	39.48	118	[2]4.1	-----	-----	77	0.3
Rock Hill	38.51	23.76	111	[3]26.3	233.33	25.90	140	[3]30.5	.5817	.0263	91	[3]12.3
Salamanca	62.55	18.44	102	[3]60.2	322.16	29.68	130	[3]20.1	-----	-----	79	0.4
Upton	313.31	−50.24	106	[3]20.2	362.72	18.94	137	[3]55.1	1.3815	.0082	91	[3]33.6

	Hydrogen (*Y*) vs Sulfate (*X*)				Hydrogen (*Y*) vs Nitrate + Sulfate (*X*)			
Station	*a*	*b*	*N*	100R^2	*a*	*b*	*N*	100R^2
Albany	0.663	−0.0667	134	[3]57.6	-----	-----	88	0.7
Athens	.195	.2444	129	[3]11.0	-----	-----	94	.0
Canton	----	----	124	.1	-----	-----	78	.7
Hinckley	.315	.0246	136	[3]11.4	0.4397	0.0076	95	[3]26.7
Mays Point	.128	.0260	140	[2]3.0	-----	-----	100	1.4
Mineola	----	----	112	1.3	-----	-----	77	.4
Rock Hill	.140	.0342	130	[2]3.4	-----	-----	90	1.6
Salamanca	.163	.0344	122	[3]6.4	-----	-----	80	2.0
Upton	.523	.0128	121	[3]41.1	.4303	.0094	88	[3]36.2

[1] Indicates statistical significance $\alpha<0.10$.

[2] Indicates statistical significance $\alpha<0.05$.

[3] Indicates statistical significance $\alpha<0.01$.

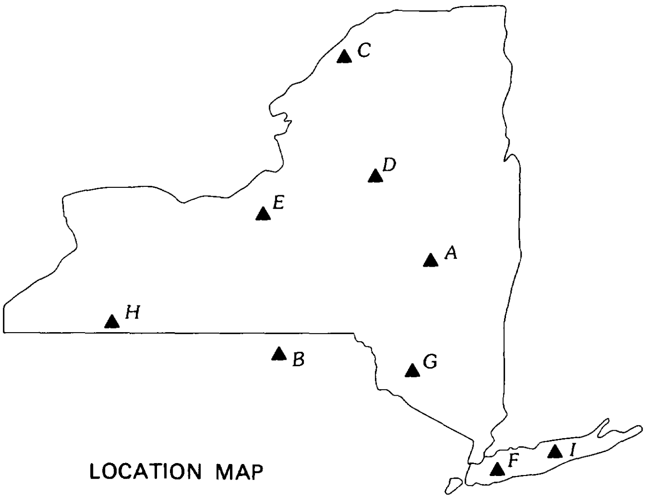

Figure 3.—Continued.

Table 5.—Results of linear regression analysis for precipitation constituent against time

[Average percent slope (trend per year) is calculated by dividing the slope (*a*-coefficient) by the mean value in table 3. *N* is number of observations.

A. Precipitation quantity

[Equation is of the form $Y=aX+b$, where Y is quantity per year, in centimeters, and X is calendar year minus 1900]

Station	*a*	*b*	*N*	$100R^2$	Average percent slope
Albany	0.277	−11.41	147	[2]4.0	3.2
Athens	.259	−11.26	149	[3]5.5	3.5
Canton	.195	−6.24	138	[1]2.5	2.5
Hinckley	.194	−3.29	159	[2]2.9	1.8
May Point	----	----	155	1.7	--
Mineola	.392	−18.18	121	[3]5.6	4.0
Rock Hill	.295	−11.09	144	[2]4.4	2.9
Salamanca	.178	−2.66	144	[1]2.0	1.7
Upton	.185	−3.14	146	[1]2.0	1.8

B. pH

[Equation is of the form $Y=aX+b$, where Y is pH and X is calendar year minus 1900]

Station	*a*	*b*	*N*	$100R^2$
Albany	-----	-----	143	0.2
Athens	-----	-----	145	0.3
Canton	0.0088	4.344	135	[2]3.6
Hinckley	−.0093	4.831	148	[3]7.5
Mays Point	-----	-----	144	1.0
Mineola	.0244	4.022	118	[3]12.2
Rock Hill	.0121	4.070	141	[3]6.7
Salamanca	−.0123	5.098	130	[2]4.6
Upton	-----	-----	134	0.0

C. Sulfate-ion concentration

[Equation is of the form $Y=aX+b$, where Y is concentration, in milliequivalents per liter, and X is calendar year minus 1900]

Station	*a*	*b*	*N*	$100R^2$	Average percent slope
Albany	−0.0015	0.2057	134	[2]3.9	−1.0
Athens	.0009	.0900	130	[1]2.8	.7
Canton	-----	-----	124	0	--
Hinckley	-----	-----	136	1.8	--
Mays Point	-----	-----	139	.2	--
Mineola	−.0014	.1880	115	[2]3.6	−1.1
Rock Hill	-----	-----	130	0	--
Salamanca	-----	-----	121	0	--
Upton	−.0008	.1081	123	[3]7.7	−1.1

D. Nitrate-ion concentration

[Equation is of the form $Y=aX+b$, where Y is concentration, in milliequivalents per liter, and X is calendar year minus 1900]

Station	*a*	*b*	*N*	$100R^2$	Average Percent slope
Albany					
Total period	-----	-----	133	0.0	---
pre-1969	-----	-----	38	2.5	---
post-1969	-----	-----	95	.2	---
Athens					
Total period	0.0065	−.4248	126	[3]15.9	12.9
pre-1969	-----	-----	27	3.8	---
post-1969	.0038	−.2266	99	[3]8.8	6.7
Canton					
Total period	.0030	−.1795	117	[3]12.1	7.6
pre-1969	.0071	−4651	32	[2]16.5	47.3
post-1969	-----	-----	85	0	---
Hinckley					
Total period	.0025	−.1525	133	[3]13.4	7.6
pre-1969	-----	-----	24	8.4	---
post-1969	-----	-----	109	1.4	---
Mays Point					
Total period	.0043	−.2634	143	[3]14.5	10.3
pre-1969	.0082	−.5378	33	[2]13.4	53.2
post-1969	-----	-----	110	1.3	---
Mineola					
Total period	.0014	−.0185	119	[3]37.7	3.8
pre-1969	-----	-----	37	.2	---
post-1969	-----	-----	82	.3	---
Rock Hill					
Total period	.0023	−.1369	120	[3]11.5	7.7
pre-1969	-----	-----	23	9.3	---
post-1969	-----	-----	97	.6	---
Salamanca					
Total period	-----	-----	122	1.8	---
pre-1969	-----	-----	26	.6	---
post-1969	-----	-----	96	1.0	---
Upton					
Total period	.0021	−.1249	139	[3]27.9	7.9
pre-1969	-----	-----	38	5.3	---
post-1969	.0007	−.0227	101	[1]2.7	2.1

[1] Indicates statistical significance $\alpha<0.10$

[2] Indicates statistical significance $\alpha<0.05$

[3] Indicates statistical significance $\alpha<0.01$

the concentration of the hydrogen ion. The pattern most evident in these graphs is that as precipitation quantity increases, both sulfate and calcium decrease, but the decrease in calcium is slightly more pronounced. The samples from Athens (fig. 3*B*) are an exception, as pointed out earlier, because the anomalously high concentrations of ammonium contributed as much as did calcium to the reaction or exchange with hydrogen, resulting in neutralization of acid. The Upton samples (fig. 3*I*) were also unique in that the decrease in acid-forming anions exceeded the decrease in neutralizing cations, which caused a net decrease in hydrogen concentration with increasing precipitation. The Upton results reflect the local coastal conditions of little contribution from dust and large contributions of sodium and chloride from sea salt.

Temporal Trends

Linear Regression

The initial form of data analysis was the simple linear regression of precipitation quantity and chemistry against time. Results are given in table 5; the corresponding historical values of precipitation quantity, pH, sulfate, and nitrate, and their regression lines for each station, are given in figures 5-8.

A linear representation is not necessarily the form that most accurately reveals the change that actually occurs. For example, a constant rate of increase in chemical concentration would result in an exponential curve, whereas a period of rapid increase followed by gradual increase would produce an S-shaped curve. Also, minor perturbations reflecting storms or dry weather, as well as normal seasonal variations, would cause fluctuations in the data that would mask long-term trends. One effect of imposing a linear fit may be to exaggerate the predicted values representing the beginning and end of the period of record. For example, applying a linear fit to data representing a constant rate of increase in concentration with time would cause the line to fall below the data cluster at the beginning and end of the graph and above it in the middle.

Because the assumptions underlying the least-square relationships were not well satisfied by the data, the concentrations calculated from these relationships should be interpreted with caution. For example, even though the slopes of chemical concentrations plotted as a function of time may be compared among one another to discern direct relationships, hydrogen concentration is non-normally distributed and yielded many near-zero values that would have affected the slope of a linear regression, thus making trends difficult to discern. The application of linear regression analysis to hydrogen concentration would, therefore, violate the test assumptions and possibly produce an unreliable result. To obtain a more reliable analysis, a linear trend in pH, rather than hydrogen ion concentration, was assessed.

Results of the linear regression analyses suggest that nitrate increased at eight of nine stations over the sampling period (fig. 8). As mentioned previously, however, the analytical technique for nitrate changed in the spring of 1969. Although the effects of this change on accuracy and precision of the data are unknown, data before 1969 seem to be drawn from a different population than those after 1969 (fig. 8); this has also been suggested by Miller and Everett (1979). Only two of nine stations show significant trends at the 0.1 level after the spring of 1969, and two stations show trends before this time (fig. 8, table 5).

The results of the linear regression analyses suggest that sulfate decreased at three of the nine stations and increased at one (fig. 7). pH increased at only two stations and decreased at three. However, a trend in pH cannot be derived from the linear trends in concentration of sulfate and nitrate, which are the acid-forming anions.

In addition, figure 5 indicates a 2- to 3-percent average annual increase in precipitation quantity during 1965-78, although little or no increase is indicated by longer periods of record. For example, the average annual increase at Albany since 1900 has been only 0.2 percent (fig. 9). The lack of detectable change in pH at some stations and a decrease in pH, as observed at six sites in the central and western part of the State, coupled with a 2- to 3-percent average annual increase in precipitation, has resulted in an increase in loading of hydrogen ions. The relationship between concentration and precipitation quantity as noted in figures 3 and 4, coupled with the change in precipitation quantity with time (fig. 9) and possible seasonal variations in constituent concentrations, further reduce the reliability of these linear trends. The seasonal Kendall test is more robust and attempts to account for these factors in addition to lack of normality (Hirsh and others, 1982).

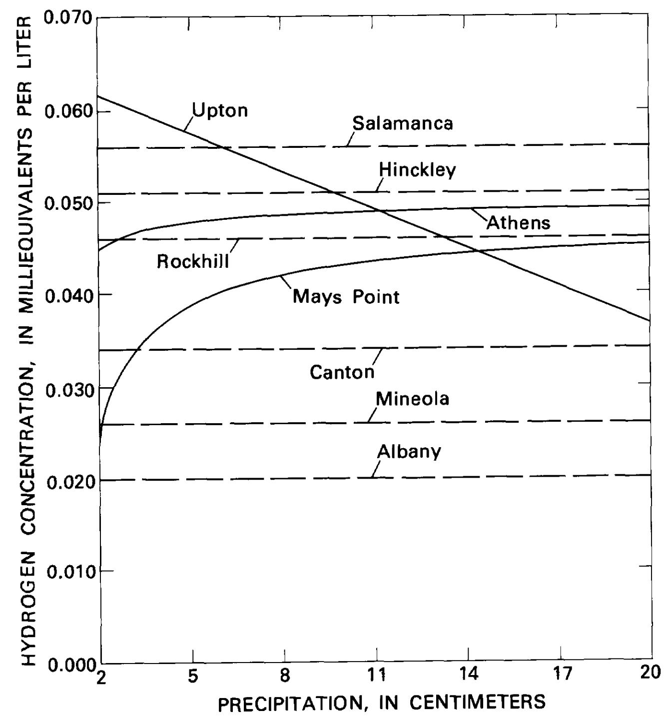

Figure 4.—Relationship between hydrogen concentration and precipitation quantity, 1965–78, at all stations. Dashed lines indicate that a relationship is statistically insignificant at $\alpha<0.1$. Where no significant relationship exists at the 0.1 level, mean concentration is shown as a horizontal (dashed) line.

Nonparametric Seasonal Kendall Test

Results of the seasonal Kendall test (table 6) generally agree with those obtained from the linear regression in table 5, although magnitudes of the trends differ somewhat, and a greater number of statistically significant trends results from the seasonal Kendall test. Also, the nine-station average sulfate trend obtained from the parametric test exceeded that of the nonparametric test by 1.5 (μeq/L)/yr.

Temporal trends of constituents having common sources, such as calcium and magnesium from dustfall, are virtually identical at a given station. However, the trend for hydrogen ion, a net result of several other fac-

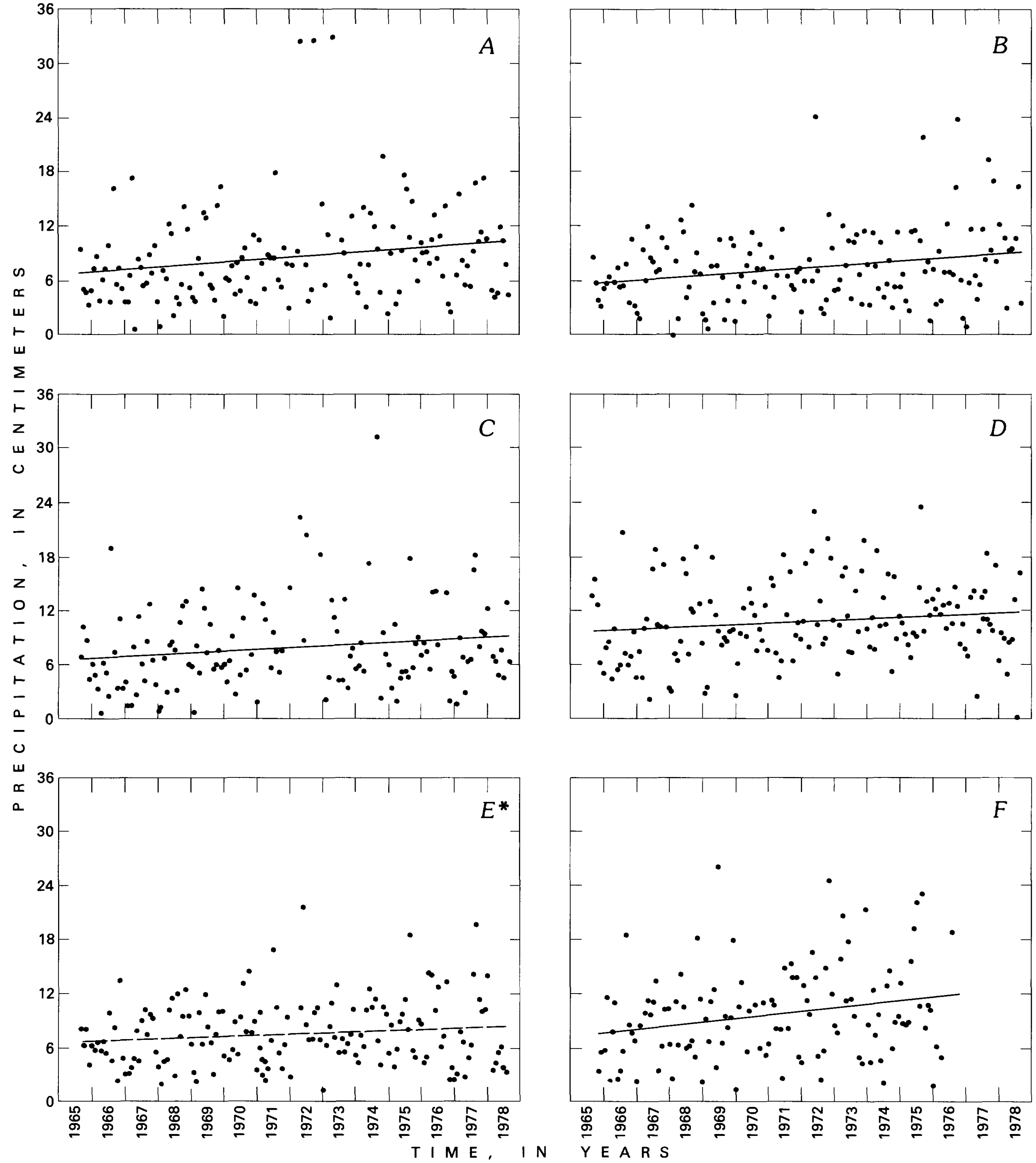

Figure 5.—Temporal trend in monthly atmospheric precipitation quantity, 1965-78, based on least-squares fit of data. Dashed line (denoted by asterisk after letter on figure) indicates trend is not statistically significant at $\alpha<0.1$. *A*, Albany. *B*, Athens. *C*, Canton. *D*, Hinckley. *E*, Mays Point. *F*, Mineola. *G*, Rock Hill. *H*, Salamanca. *I*, Upton.

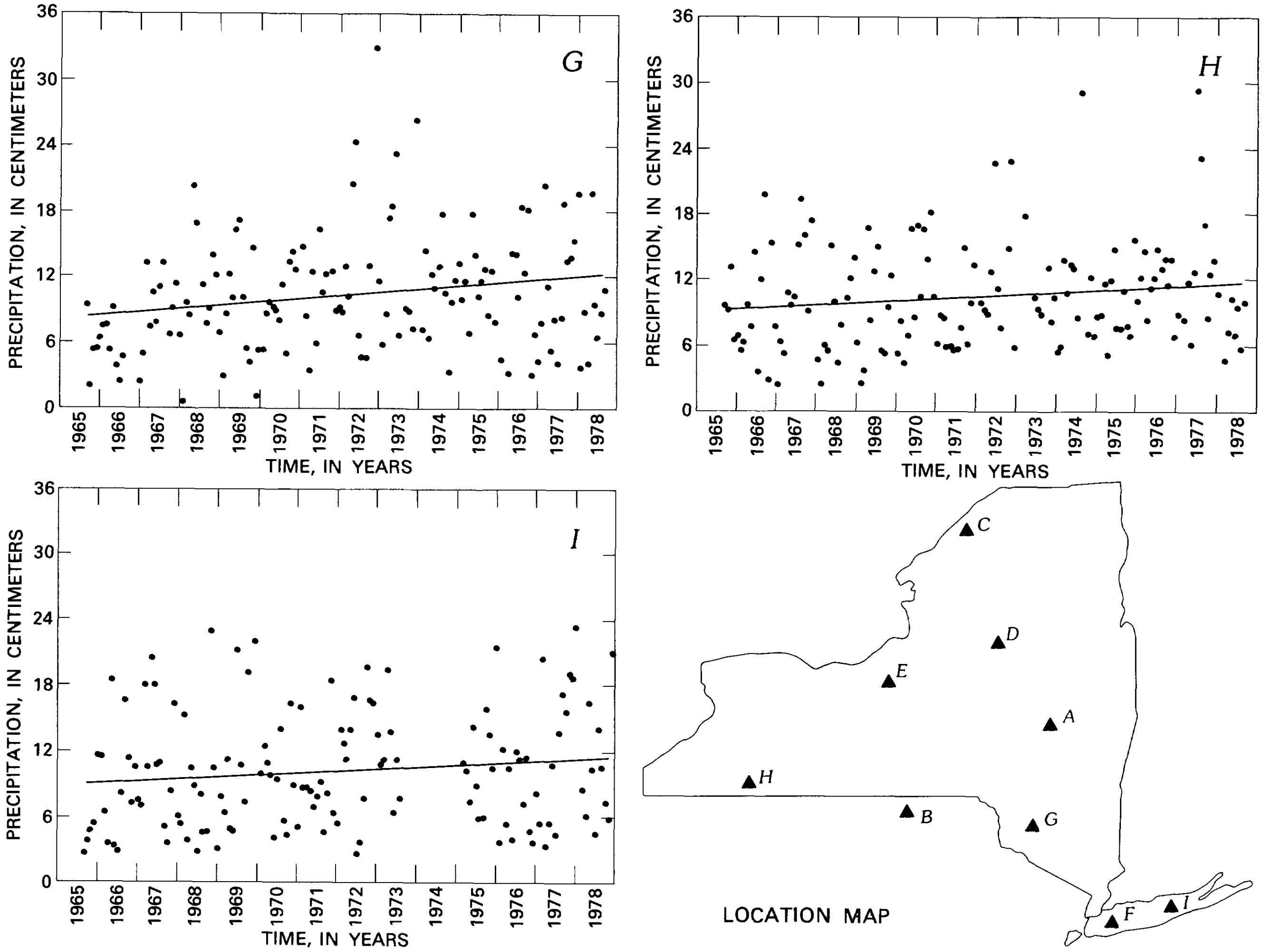

Figure 5.—Continued.

tors, cannot be predicted as readily. By a procedure analogous to Granat's (1972) estimate of hydrogen-ion concentration (table 3), hydrogen trend was calculated from the difference between anion and cation trends. Comparison of calculated hydrogen-ion trends with measured trends showed generally poor agreement. At six of the nine stations, differences exceeding (1 μeq/L)/yr were observed. At Hinckley, Mays Point, and Salamanca, a decrease in hydrogen ion was calculated, but the Kendall test results suggest an increase. At Mineola and Rock Hill, the opposite was observed. Changes in bicarbonate (alkalinity) over the period of record could explain these differences. If bicarbonate increased at Rock Hill and Mineola, correlative with the increases in base cations (calcium, sodium, magnesium, and potassium), a decrease in hydrogen would be expected. Similarly, if bicarbonate decreased at Hinckley, Mays Point, and Salamanca, an increase in hydrogen, as indicated by the Kendall test results, would be expected.

Records from three stations (Albany, Athens, and Upton) show no statistically significant trend in hydrogen-ion concentration. In contrast, Hinckley, Mays Point, and Salamanca show a statistically significant increase ranging from 3 to 6 percent, and the remaining stations (Canton, Mineola, and Rock Hill) show a comparable decrease. As a whole, these trends balance out to suggest that pH of precipitation in New York has not changed since 1965, although station-to-station comparisons reveal significant local differences.

The increase in hydrogen ion at Hinckley, Mays Point, and Salamanca would suggest a decrease in pH in the western and central part of New York, whereas the hydrogen-ion decrease at Canton, Mineola, and Rock Hill would suggest an increase in pH in the southeastern and northeastern part. One factor may be proximity to the industrialized Midwest, a major source of acid airborne emissions and a general west-to-east transport by wind. Cogbill and Likens (1974), in their central New York study, noted that pH of wetfall originating in air

Table 6.—Results of temporal-trend analysis of precipitation data based on nonparametric seasonal Kendall test

[Functional equations for *f*(*Q*) are based on relationships between chemical concentration and precipitation quantity displayed in figs. 3*A*–*I*, where M = mean, L = linear, and H = hyperbolic. Nitrate trends calculated for data after spring of 1969. For chemical concentrations, slope is trend, in milliequivalents per liter per year. Average percent slope is calculated as slope divided by mean in table 3.]

Station	Hydrogen			Calcium			Magnesium			Sodium			Potassium		
	Slope	Average percent slope	f(Q)	Slope	Average percent slope	f(Q)	Slope	Average percent slope	f(Q)	Slope	Average percent slope	f(Q)	Slope	Average percent slope	f(Q)
Albany	----	----	--	−0.0045	[3]−3.2	L	----	----	--	----	----	--	----	----	--
Athens	----	----	--	.0016	[2]2.9	L	0.0007	[3]5.0	L	----	----	--	0.0002	[1]2.9	L
Canton	−0.0011	[2]−3.2	M	.0015	[2]2.2	L	.0012	[3]4.8	L	----	----	--	----	----	--
Hinckley	.0018	[3]3.5	M	----	----	--	----	----	--	−.0003	[2]−3.0	H	----	----	--
Mays Point	.0015	[2]3.8	H	----	----	--	----	----	--	----	----	--	----	----	--
Mineola	−.0019	[3]−7.3	M	.0022	[2]2.6	H	.0022	[2]4.9	H	----	----	--	----	----	--
Rock Hill	−.0020	[3]−4.3	M	.0012	[2]2.8	L	.0008	[1]1.9	M	----	----	--	.0004	[1]2.0	M
Salamanca	.0035	[3]6.3	M	----	----	--	----	----	--	−.0013	[2]−8.9	H	----	----	--
Upton	----	----	--	----	----	--	----	----	--	----	----	--	----	----	--

[1] Indicates statistical significance α0.10.

[2] Indicates statistical significance α0.05.

[3] Indicates statistical significance α0.01.

masses with a western component was lower by 0.25 units than wetfall originating in air masses with a southern or northern component. The Canton (northeastern) station might be less likely to receive storms with a western component than would Salamanca, Mays Point, or Hinckley. This may be only a partial explanation, however. For example, the sum of calcium, magnesium, and sodium in bulk samples decreased at stations where hydrogen-ion concentrations increased, and their sum increased where hydrogen decreased. Thus, geographic differences in hydrogen-ion trends may be partly attributed to local trends in base-neutralizing dryfall.

Nitrate concentrations increased at only three of the nine stations. Two of these stations, Hinckley and Upton, at mentioned previously, have the lowest total ion concentrations, and are, therefore, the most sensitive to changes in precipitation chemistry. The increase in nitrate detected from the bulk precipitation data at these stations, however, is insufficient to suggest a regional nitrate increase.

Trends in sulfate concentrations during the period studied are definable; sulfate decreased 1–4 percent per year at seven of the nine stations. These trends compare favorably with those derived by Cogbill and Likens (1974) from a combination of measured and calculated data. Although results from that study indicate that the amount of acid-forming nitrate ion increased from 22 percent of the total acid-forming anions in 1955 to 30 percent in 1973, the pH in central New York remained the same, chloride increased from 0 to 5 percent, and sulfate decreased from 78 to 65 percent during the same interval.

Although the ratio of nitrate to nitrate plus sulfate in the Geological Survey network exceeded that in Cogbill and Likens' (1974) study by several percent, this difference may not be important because it may result from differences in method of collection (wetfall versus bulk) and chemical and biological alteration during the 1-month storage period in the field.

The data obtained suggest a slight decrease in sulfate concentration within the State. A reduction in the burning of wood and coal and a corresponding increase in the use of cleaner petroleum should have produced a decrease in sulfate, but this trend has been counterbalanced by an increased consumption of fuel, a decrease in the release of coal ash (a neutralizing component), and possibly the removal of all but the gaseous acid component by scrubbers on tall smokestacks. The data in table 6 also indicate an increase in ammonium concentrations. Whether the ammonium increase results from human activity such as use of anhydrous ammonia and urea fertilizers or from natural biological processes is not known; its subsequent oxidation at Athens may partly account for the increasing trend in nitrate there.

Surface Water

Surface water is more difficult to interpret in terms of chemical character than precipitation because it is influenced by many more factors. Where the terrain is unreactive to water, chemical composition of the water will be similar to that of atmospheric deposition, but where the rocks are reactive, the water will be affected by a complex series of reaction equilibria and kinetics. Urbanization may further complicate the chemical composition of surface water by its contributions of urban runoff, industrial waste, sediment from construction, and sewage; also, agriculture may affect the chemical composition of surface waters by increasing the weathering rate of soils, contributing animal wastes, and adding soluble chemical components from fertilizers.

Table 6.—Continued

Ammonium			Nitrate			Sulfate			Chloride			Total ions		
Slope	Average percent slope	f(Q)	Slope	Average percent slope	f(Q)	Slope	Average percent slope	f(Q)	Slope	Average percent slope	f(Q)	Slope	Average percent slope	f(Q)
----	----	--	----	----	--	−0.0054	[3]−3.4	H	----	----	--	----	----	--
0.0067	[3]10.6	L	0.0044	[3]8.7	H	.0033	[3]2.5	L	0.0011	[3]4.2	L	0.0202	[3]5.2	L
.0008	[1]3.5	H	----	----	--	----	----	--	----	----	--	.0087	[3]2.5	H
.0012	[3]6.3	H	.0017	[2]5.0	H	−.0015	[2]−1.8	H	----	----	--	----	----	--
.0010	[3]5.0	H	----	----	--	−.0018	[2]−1.6	H	----	----	--	.0068	[3]1.8	H
.0033	[3]10.3	L	----	----	--	−.0052	[3]−4.0	H	----	----	--	.0080	[1]1.7	L
.0009	[2]4.5	H	----	----	--	----	----	--	.0007	[2]2.6	L	.0093	[3]2.8	L
----	----	--	----	----	--	−.0021	[1]−1.5	M	----	----	--	----	----	--
.0003	[1]2.7	H	.0004	[1]1.3	L	−.0026	[3]−3.5	H	----	----	--	----	----	--

[1] Indicates statistical significance $\alpha 0.10$.

[2] Indicates statistical significance $\alpha 0.05$.

[3] Indicates statistical significance $\alpha 0.01$.

Chemical Composition

Urbanization and agriculture both have major effects on chemical composition of streams, as evidenced by a comparison of the mean concentrations of chemical constituents (table 7) of Buffalo Creek basin (the most urbanized basin studied) and Black Creek basin (an agricultural basin) with those of the least disturbed basins—the East Branch of the Sacandaga River and Esopus Creek (fig. 1; table 2). Total ion concentration of Buffalo Creek and Black Creek was 7.50 meq/L and 21.71 meq/L, respectively, which is 8 to more than 20 times greater than concentrations in the undisturbed streams.

Because only one basin, Buffalo Creek, has a significant percentage of urbanization (table 2), it was difficult to compare the effect of agriculture with the effect of urbanization, but a general pattern of increasing total ion concentration with increasing percentage of agricultural land use is evident. A graph of total ion concentration (meq/L) against specific conductance (fig. 10) depicts the effects of agriculture on surface-water quality. The numbers next to the data points in figure 10 correspond to the station numbers listed in table 2, and, as the distribution of data indicates, total ion concentration and specific conductance generally increase with percentage of agricultural land use. Small exceptions to this trend are apparent in the intermediate percentage range, represented in figure 10 by the drainage basins of Gridley Creek (4), Fivemile Creek (5), Conewango Creek (6), and Buffalo Creek (7), which are 47, 39, 48, and 47 percent agricultural, respectively. Slight deviations from the general trend at these stations suggest that the type and degree of agriculture influences the general effect on chemical composition of surface water within a basin. Although Black Creek basin (7) has the same percentage of agricultural land use as Gridley Creek (4) and Conewango Creek (6) basins, the higher mean total ion concentration in Black Creek (table 7) was attributed to the higher percentage of urban land use (table 2).

From these observations, it may be inferred that the geologic character of a basin is less important than land use in determining the overall chemical composition of surface waters. The major anions in surface waters, in order of decreasing concentration, typically were bicarbonate, sulfate, and chloride. The exception was the East Branch of Sacandaga River, in an Adirondack region underlain by resistant bedrock (fig. 1), where the dominant anion was sulfate followed by bicarbonate (table 7). Mean pH of this river was 6.8, significantly less than that of the other streams studied. The low bicarbonate and high sulfate concentrations of precipitation at an adjacent site (Hinckley, fig. 1, table 3) suggest a similarity between precipitation quality and surface-water chemistry in this region.

The highest observed nitrate concentrations of surface water were in Buffalo Creek, the most urbanized basin, where mean nitrate concentration was more than an order of magnitude higher than in Black Creek, the most agricultural basin. The high nitrate concentrations in Buffalo Creek are attributed to sewage treatment and disposal. Nitrate concentrations at the remaining seven stream stations were comparable to, or slightly lower than, those in bulk monthly precipitation samples from nearby stations.

Relationship Between Chemical Composition and Discharge

Linear, hyperbolic, and general hyperbolic relationships between chemical concentration and discharge of surface water are listed by site and constituent in table 8; also given are β values (a constant related to

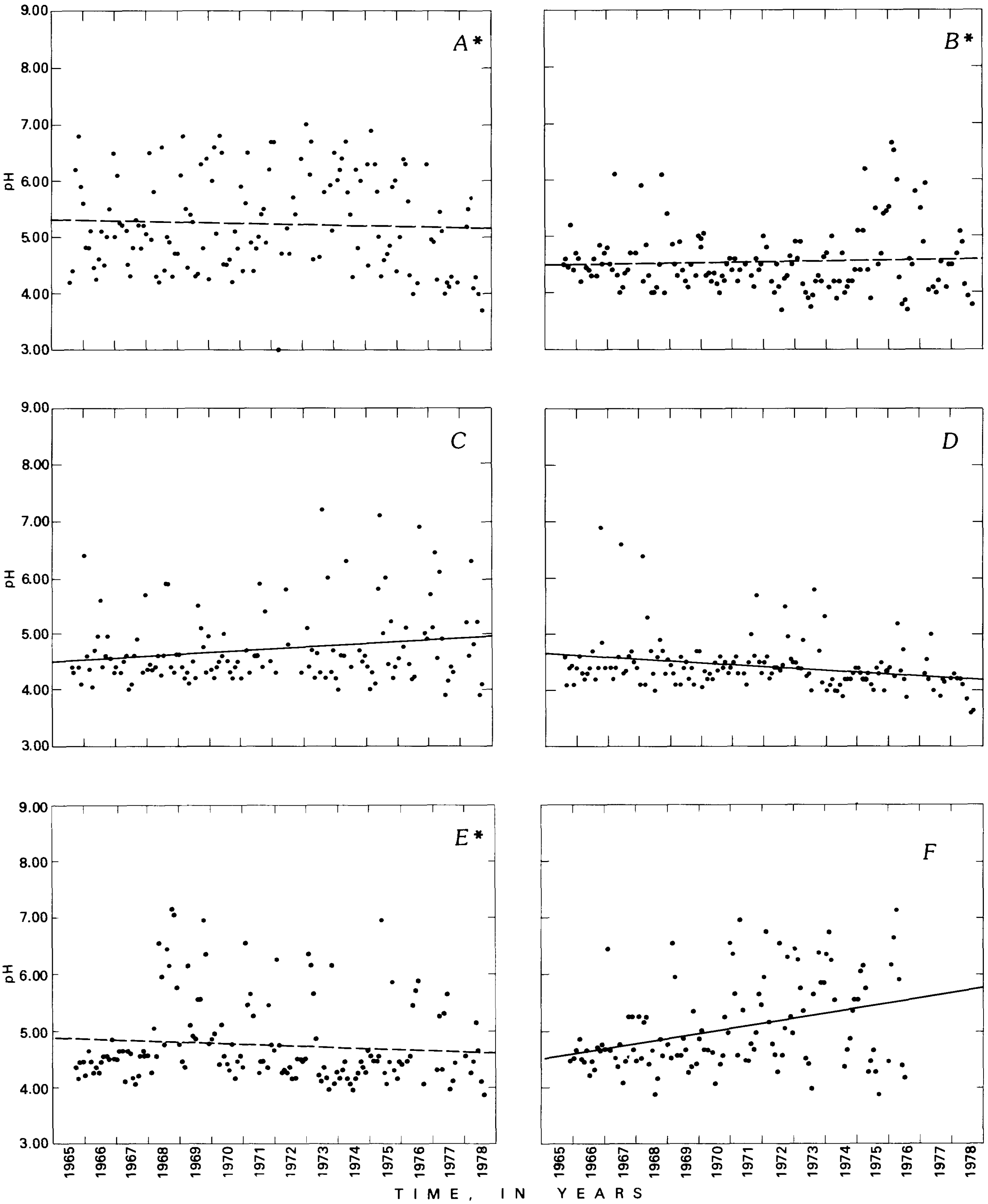

Figure 6.—Temporal trend in pH of atmospheric precipitation, 1965-78, based on least-squares fit of data. Dashed line (denoted by asterisk after letter on figure) indicates trend is not statistically significant at $\alpha < 0.1$. *A*, Albany. *B*, Athens. *C*, Canton. *D*, Hinckley. *E*, Mays Point. *F*, Mineola. *G*, Rock Hill. *H*, Salamanca. *I*, Upton.

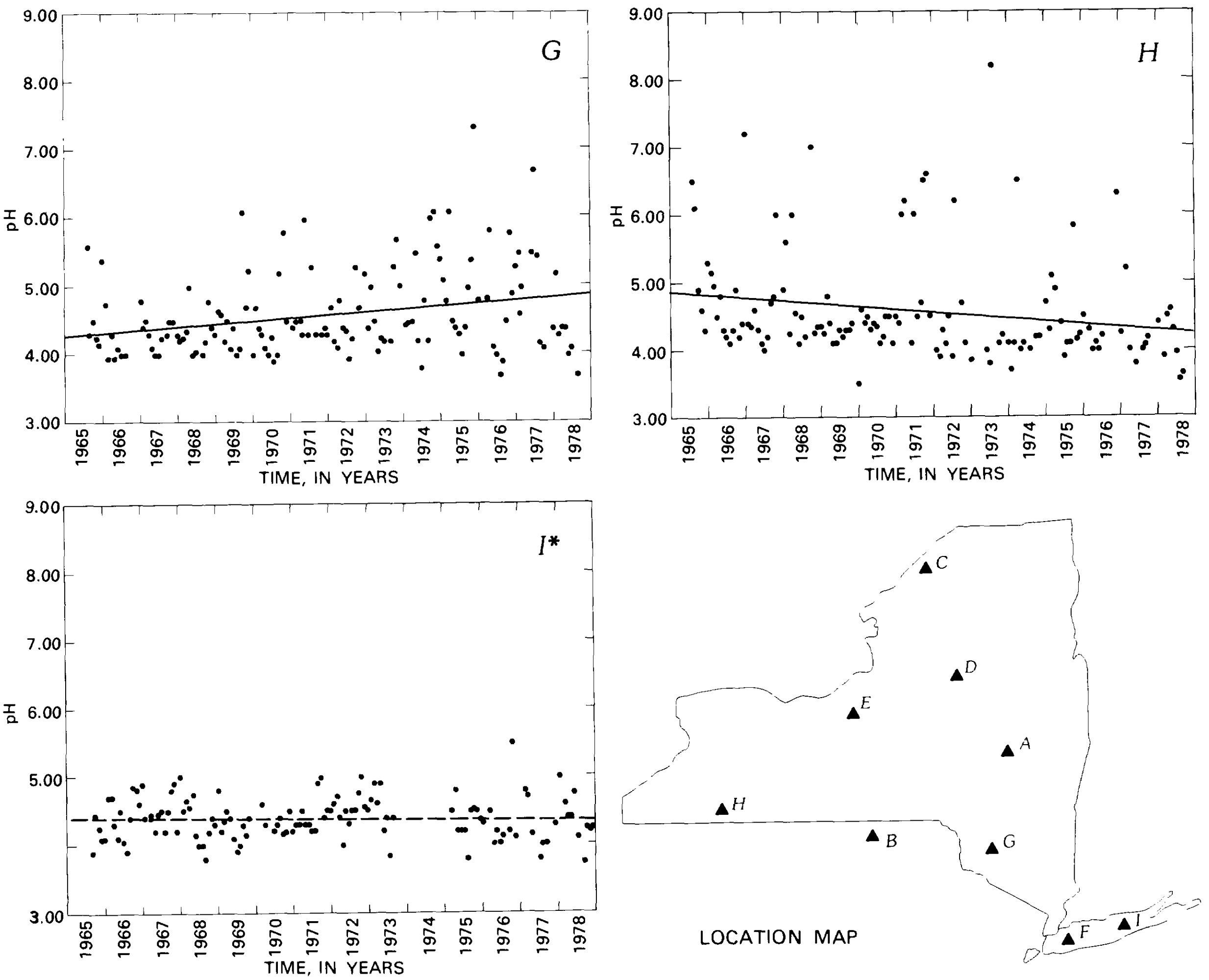

Figure 6.—Continued.

residence time of water) for the general hyperbolic relationship and the R^2 value with the corresponding significance level. The relationship of concentration to discharge was determined through the linear, hyperbolic, and general hyperbolic equations (eqs 1, 2, 3), with discharge treated in units of cubic meters per day per square kilometer [$(m^3/d)/km^2$] to facilitate comparison with results from a similar study of watersheds in the Hubbard Brook Experimental Forest, N.H. (Johnson and others, 1969). The general hyperbolic equation (eq 3), which was devised to incorporate the mixing of ground water and surface water (Johnson and others, 1969), produced significantly better results than did the simpler linear or hyperbolic relationships (eqs 1, 2). Of the 81 possible relationships of concentration to discharge (nine constituents at each of nine stations), 61 were general hyperbolic, 4 were linear, 2 were hyperbolic, and 14 showed no significant pattern.

The β term in the general hyperbolic equation (eq 3) is defined by the limit, as stream discharge approaches zero, of the residence time of water in a basin divided by the volume of water per unit area and may be regarded as a constant related to the residence time of water in a basin. Streams draining the glaciated sedimentary strata of western and central New York generally have a relatively high ground-water storage potential, especially those in areas of low relief adjacent to the Great Lakes, and therefore are likely to have much lower β values than do streams draining the Adirondack area, which respond rapidly to precipitation as a result of the high relief, impermeable bedrock, and low storage capacity. (See β values in table 8.)

The mean exponent (for all constituents) in the term for the East Branch of the Sacandaga River, in the center of the Adirondacks, was −3.0, which is equal to published values for watersheds in the geologically

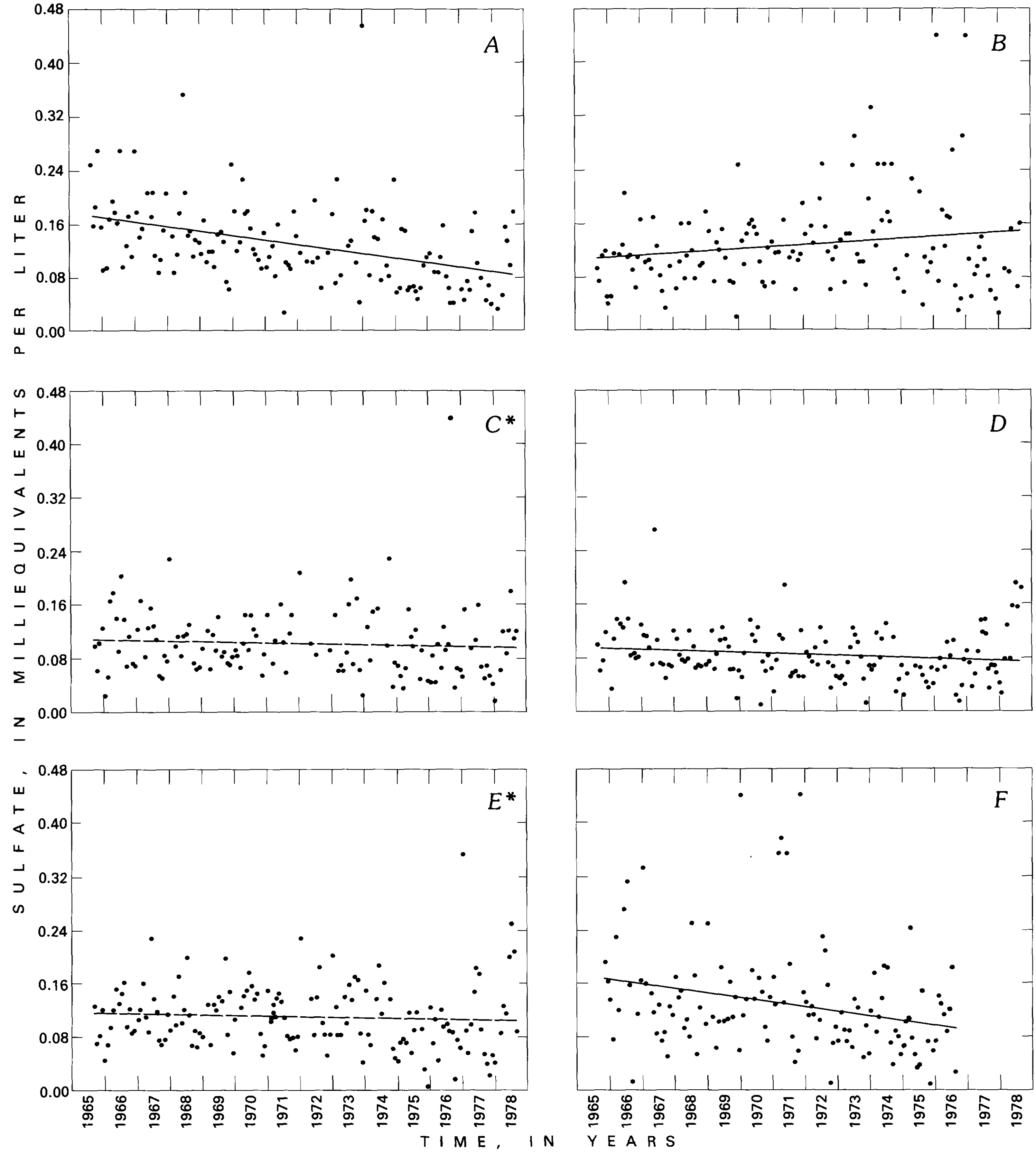

Figure 7.—Temporal trend in sulfate concentration of atmospheric precipitation, 1965–78, based on least-squares fit of data. Dashed line (denoted by asterisk after letter on figure) indicates trend is not statistically significant at $\alpha<0.1$. *A*, Albany. *B*, Athens. *C*, Canton. *D*, Hinckley. *E*, Mays Point. *F*, Mineola. *G*, Rock Hill. *H*, Salamanca. *I*, Upton.

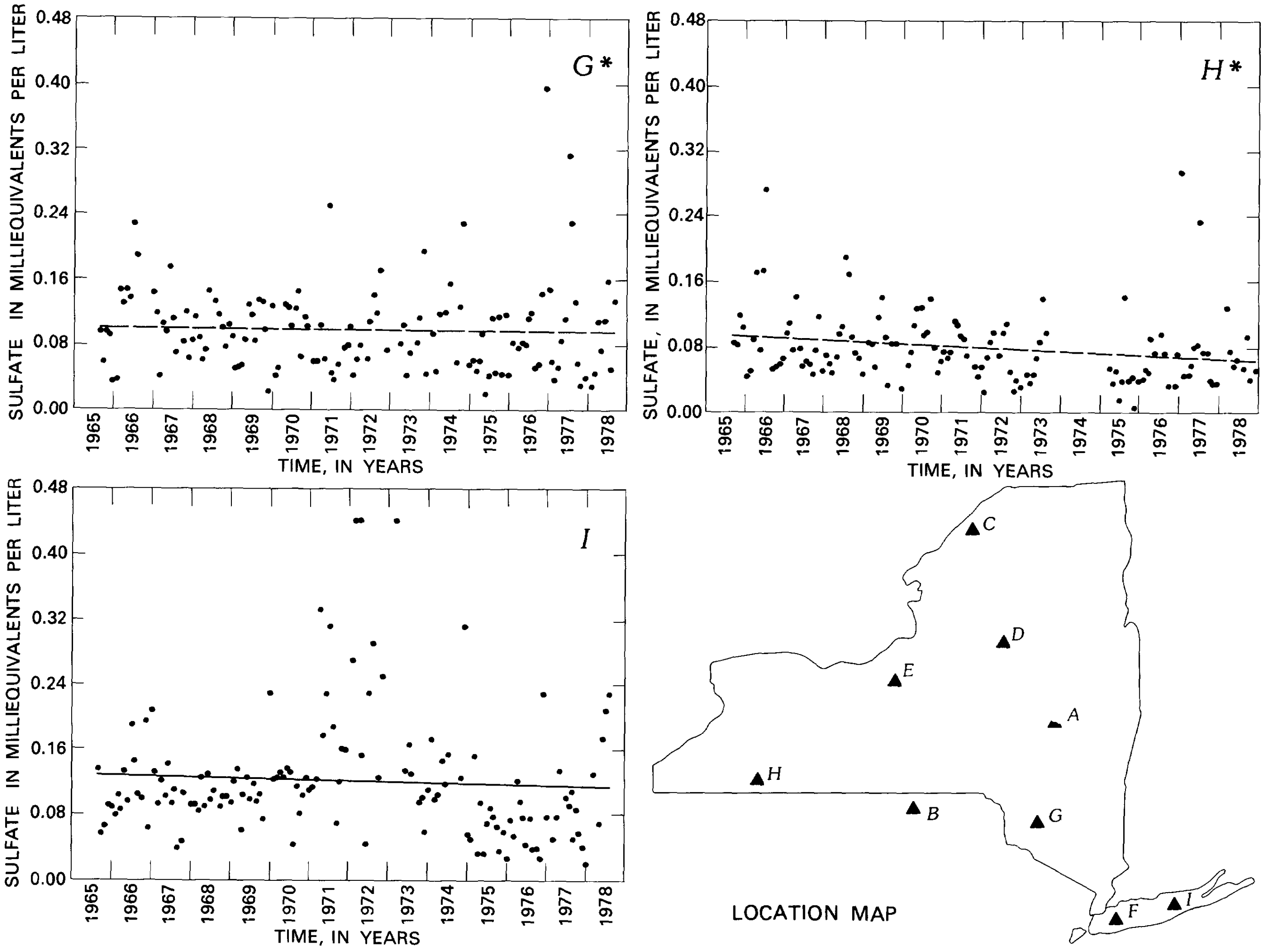

Figure 7.—Continued.

similar terrain of the Hubbard Brook Experimental Forest (Johnson and others, 1969). The lowest β values, $<10^{-4.0}$, were obtained from Buffalo Creek and Fivemile Creek in the Ontario plain, which contains glaciated sedimentary rocks and has low relief. The low β value of these basins is hypothesized to result from the large volume of water per unit area at low flow. (Low relief results in low ground-water gradients.)

The intercept term (mean concentration) in the hyperbolic equation represents the predicted concentration of a constituent as discharge approaches infinity. At high discharge, the ground-water contribution to surface-water bodies is relatively small, so that the chemical signature of surface waters will mainly reflect contributions from interactions with surface sources such as vegetation, salts, and sorption-ion exchange reactions with surficial materials. The most accurate results produced by the general hyperbolic equation were those correlating discharge with total ion concentration and specific conductance (table 8). (The accuracy of results for these two factors reflects the relationship between them; see fig. 10.)

The basins that showed the closest agreement between intercept values (concentration) derived from the general hyperbolic equation (table 8) and the mean values of total concentration and specific conductance determined from bulk monthly precipitation samples at inland sites (table 3) were those that are predominantly forested (table 2). The agricultural basins had higher intercept values than did mean monthly bulk-precipitation concentrations, which indicates significant contributions of solutes from the soils.

The most urbanized basin, Buffalo Creek, probably received many components from urban runoff; yet despite the multiplicity of sources, the general hyperbolic equation provided a close fit to the relationship between discharge and chemical concentrations. However, the large negative intercept value suggests that the close fit may be fortuitous.

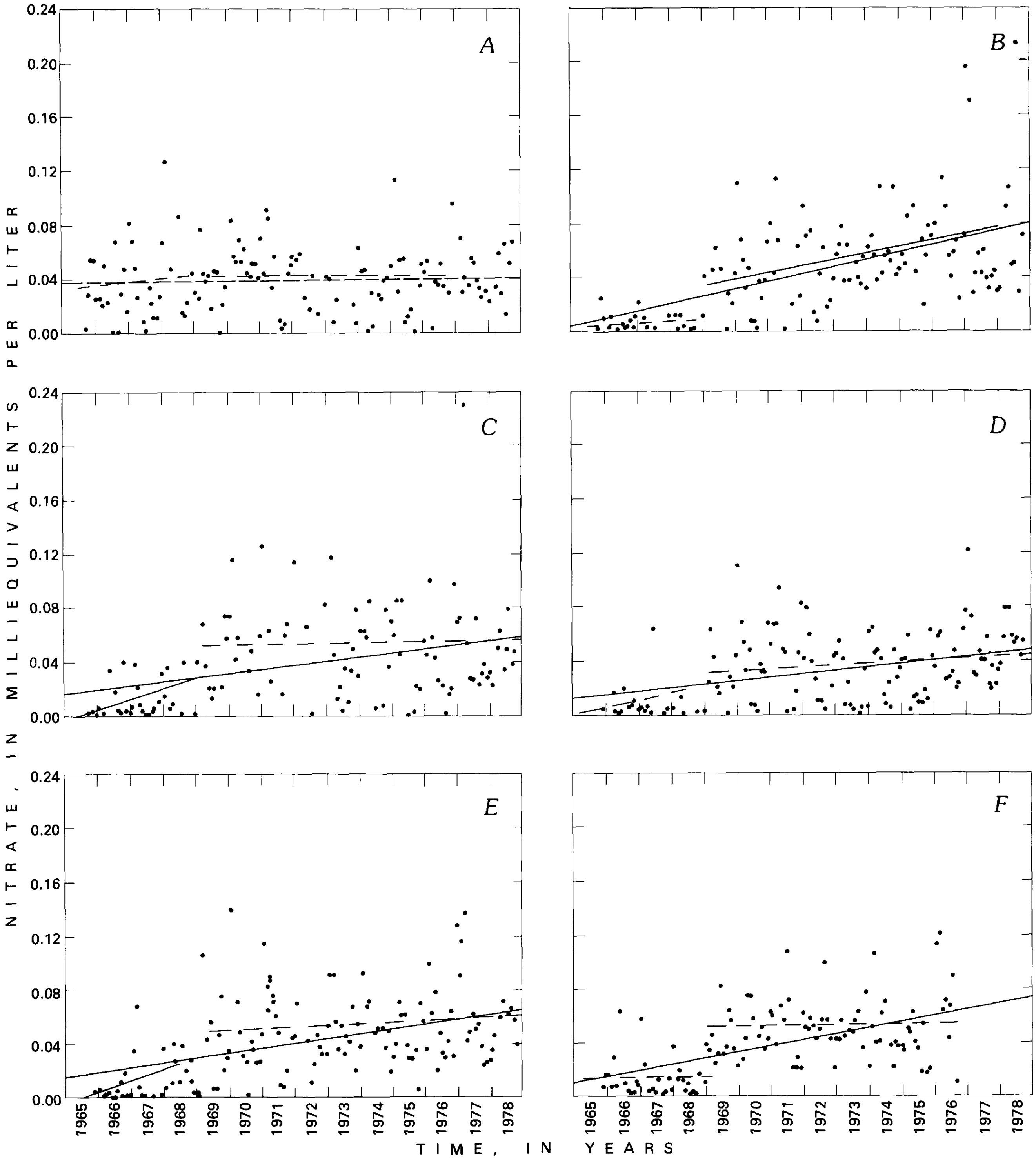

Figure 8.—Temporal trend in nitrate concentration of atmospheric precipitation, 1965-78, based on least-squares fit of data. Short lines represent period before or after spring 1969. Dashed line indicates trend is not statistically significant at $\alpha < 0.1$. *A*, Albany. *B*, Athens. *C*, Canton. *D*, Hinckley. *E*, Mays Point. *F*, Mineola. *G*, Rock Hill. *H*, Salamanca. *I*, Upton.

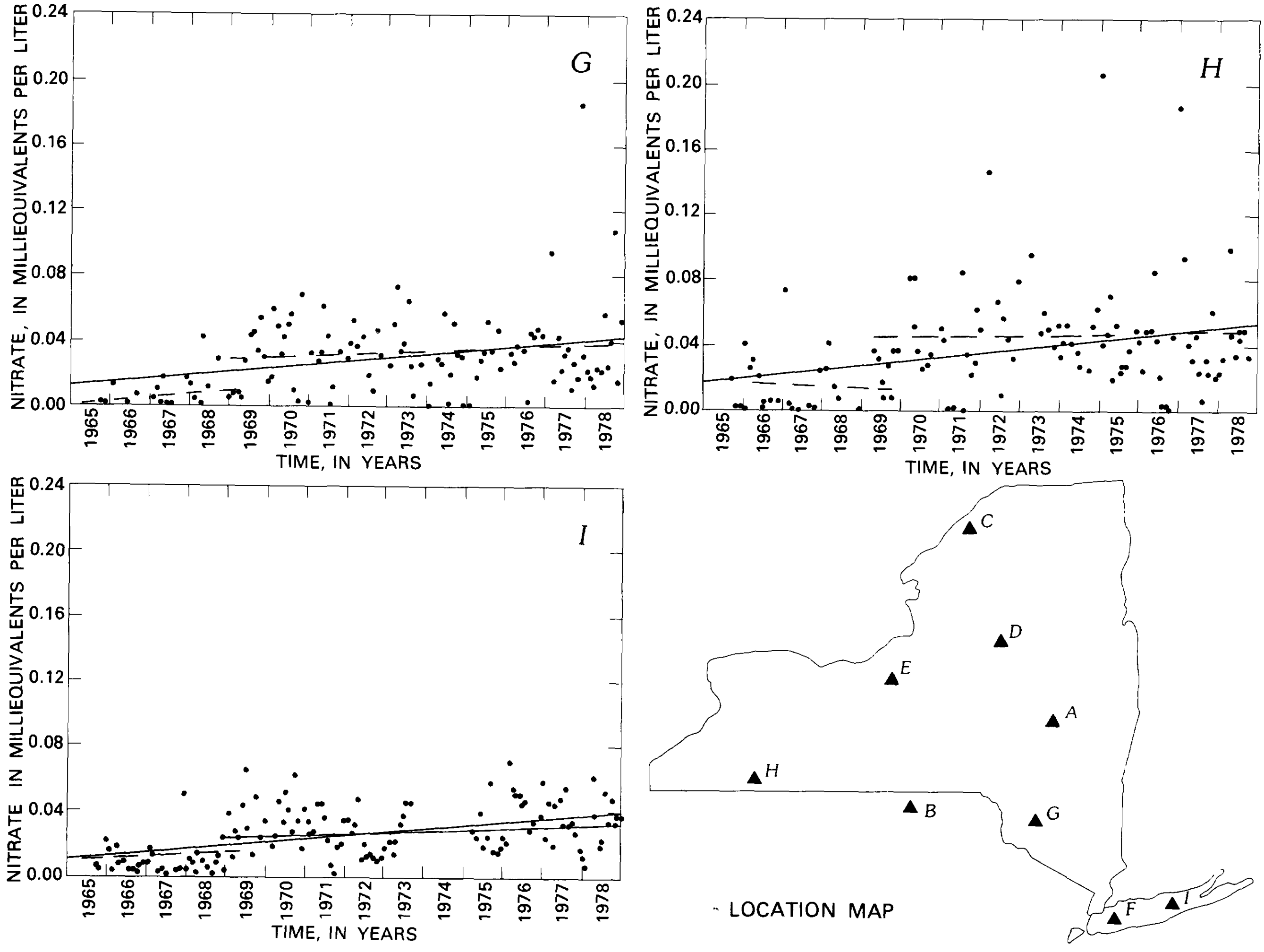

Figure 8.—Continued.

A direct relationship between hydrogen-ion concentration and discharge was indicated at all sites. This relationship (table 8) reflects, in part, the extremely small interaction of the highly acidic, dilute water held in the snowpack with the soils and rocks during the spring snowmelt.

In summary, chemical trends in surface waters are affected by both urbanization and agriculture. Urbanization alters chemical-transport rates and contributes pollutants; agricultural practices increase the chemical yield of basins by exposing fresh mineral faces and increasing sedimentation and also by adding the soluble components of fertilizers and animal wastes. However, carbonate minerals in soils and (or) bedrock mask changes in the pH of runoff through their large buffering capacity and rapid reaction rate. Thus, the only streams in which pH might show a response to temporal changes in precipitation quality are in undisturbed basins in areas having unreactive rocks and soils.

Temporal Trends

Many streams showed trends in concentration of chloride and sulfate. Five streams show a statistically significant trend in chloride concentration at the 0.1 level (table 9). These trends indicate that chloride concentration has increased an average of 2 to 7 percent per year. In addition, results of the seasonal Kendall test suggest that sulfate concentrations have decreased by an average of 1 to 4 percent Statewide in seven of the nine streams. Trends in sulfate concentrations were not detected at Gridley Creek and Oquaga Creek, possibly reflecting the shorter period of record for these streams than for the other streams (table 2). This decrease in sulfate concentration in streams is similar to that observed for precipitation (table 6) and may, therefore, reflect a decrease in sulfate from atmospheric deposition. A decrease in sulfate in headwater streams in Pennslyvania has also been observed (Ritter and Brown, 1981).

Of the nine basins studied, only the East Branch of the Sacandaga River is characterized by crystalline bedrock and little disturbance; the rest are underlain by sedimentary rocks containing carbonate minerals and have higher percentages of urbanization and agriculture. Chemical analyses of the East Branch of the Sacandaga River (table 9) indicate significant trends in concentration of nitrate, sulfate, chloride, total ions, and alkalinity but no discernible trends in hydrogen-ion concentration. One explanation may be that trends in the two acid-forming anions (nitrate and sulfate) offset each other; nitrate increased 0.0040 (meq/L)/yr, whereas sulfate decreased 0.0041 (meq/L)/yr. These values agree with those of a similar study on the East Branch of the Sacandaga by Schofield (written commun., 1976).

Bicarbonate ion is produced from mineral weathering in soils. The higher concentration of sulfate than bicarbonate (table 7) in samples from the East Branch of Sacandaga basin suggest little interaction between precipitation and soils. Furthermore, if the decrease of sulfate in precipitation of 0.002 (meq/L)/yr is adjusted for enrichment caused by evapotranspiration, the adjusted value nearly matches the observed decreasing trend of 0.004 (meq/L)/yr (table 6). The increased hydrogen-ion loadings in precipitation with time and the small interaction of water with the soil suggest that the basin water has a low capacity to neutralize acid. This observation is supported by the stream's decrease in alkalinity of 0.083 (meq/L)/yr since 1965.

In general, hydrogen-ion concentration of surface water is a function of many geochemical and biochemical reactions, which makes it virtually impossible to relate trends to any simple cause. For example, hydrogen-ion concentration of Fivemile Creek (fig. 1) has increased 0.026×10^{-3} (meq/L)/yr since 1965, although nitrate and sulfate have decreased 5.4×10^{-3} and 10×10^{-3} (meq/L)/yr, respectively. Furthermore, alkalinity has actually increased despite the increase in hydrogen-ion concentration. Results from other basins are similarly complex, and trends are difficult to interpret, not only in terms of hydrogen ion but also in other constituents. Several trends are discernible from the data in table 9; however, it is beyond the scope of this study to evaluate their possible causes.

CONSIDERATIONS FOR FUTURE STUDIES

In 1964, when sampling of atmospheric deposition began, the use of bulk precipitation as a measure of atmospheric input was an accepted practice, and some of the problems associated with this practice were not widely recognized. For example, dry fallout when collected by a funnel loses a large fraction of the fine suspended particulates upon impact. Furthermore, much of the material settling into the collector may be locally derived, which would mask the effects of regional changes. It would be desirable to continue the stations for at least two more years with bulk collectors beside collectors that separate wetfall from dryfall. The data so obtained should help to identify the differences between dryfall and wetfall and help differentiate between local and regional influences in bulk-sample data collected in the past. Analysis of the soluble dryfall material should indicate the extent to which dryfall affects chemistry of bulk precipitation samples. Comparison of nutrients in wetfall samples with leachable nutrients from dryfall and with nutrients in refrigerated bulk samples collected monthly would establish the extent of nutrient change during storage. Such information would permit closer evaluation of the nutrient information given in this report.

The discussion of trends in stream chemistry describes the major factors that inhibit evaluation of the effect of precipitation chemistry on stream chemistry. However, it should be possible to select a few small streams and lakes in the Adirondack and Catskill Mountains and monitor precipitation and stream chemistry over the next 10 to 20 years; this could provide an adequate long-term record for assessing temporal trends.

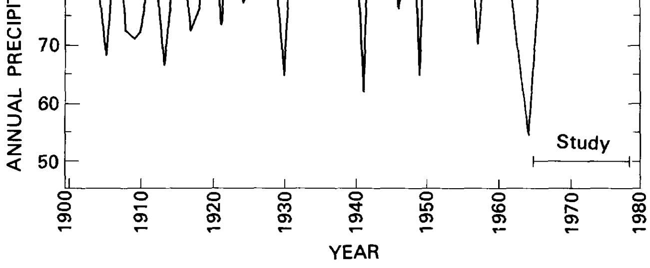

Figure 9.—Annual precipitation quantity from 1900–80 at Albany, N.Y.

Table 7.—Mean composition of surface water at sampling sites in New York

[Values are in milliequivalents per liter except as indicated; number of observations is in parentheses. Site locations are given in fig. 1]

Constituent or characteristic	East Branch Sacandaga River at Griffin	Esopus Creek at Shandaken	Oquaga Creek near Sanford	Gridley Creek above East Virgil	Fivemile Creek near Kanona	Conewango Creek at Waterboro	Buffalo Creek at Gardenville	Black Creek at Churchville	Deer Creek at Brasher Iron Works
Discharge (m^3/s)	6.91 ± 13.74 (115)	3.80 ± 4.06 (154)	0.17 ± 0.19 (67)	0.60 ± 0.88 (55)	2.24 ± 5.04 (109)	15.79 ± 17.21 (120)	5.53 ± 8.90 (105)	3.85 ± 5.39 (116)	8.25 ± 11.55 (116)
Normalized discharge [$(m^3/d)/km^2$]	2,024. ± 4,024. (115)	2,135. ± 2,275. (154)	1,182. ± 1,356. (67)	1,929. ± 2,828. (55)	1,117. ± 2,515. (109)	1,802. ± 1,964. (120)	1,281. ± 2,061. (105)	1,043. ± 1,461. (116)	1,454. ± 2,037. (116)
Hydrogen (measured)	.000206 ± .000184 (115)	.000269 ± .000465 (154)	.000321 ± .000639 (67)	.000059 ± .000058 (55)	.000026 ± .000027 (109)	.000047 ± .000029 (120)	.000017 ± .000012 (107)	.000014 ± .000009 (116)	.000046 ± .000032 (117)
pH	6.69	6.57	6.49	7.23	7.59	7.33	7.77	7.85	7.34
Specific conductance (micromho/cm at 25°C)	47.1 ± 8.0 (115)	53.7 ± 10.1 (154)	67.8 ± 20.0 (67)	197. ± 74. (55)	262. ± 76. (109)	231. ± 68. (120)	377. ± 68. (107)	1021. ± 252. (116)	132. ± 26. (117)
Alkalinity (mg/L as $CaCO_3$)	8.30 ± 3.23 (115)	11.08 ± 3.76 (151)	17.71 ± 10.27 (55)	61.07 ± 31.87 (55)	77.32 ± 32.32 (109)	80.02 ± 29.23 (120)	112.57 ± 23.26 (107)	196.12 ± 39.98 (116)	49.03 ± 10.46 (117)
Total ions	.854 ± .174 (65)	.944 ± .192 (133)	1.270 ± .403 (32)	3.636 ± 1.536 (54)	5.040$_6$1.702 (72)	4.471 ± 1.430 (86)	7.50 ± 1.38 (72)	21.71 ± 5.45 (69)	2.71 ± .51 (65)
Calcium	.267 ± .044 (101)	.270 ± .059 (152)	.361 ± .143 (39)	1.224 ± .543 (55)	1.653 ± .527 (95)	1.611 ± 0.505 (106)	2.449 ± .439 (93)	7.731 ± 2.169 (100)	.838 ± .158 (102)
Magnesium	.093 ± .050 (101)	.098 ± .020 (152)	.143 ± .058 (39)	.398 ± .177 (55)	.622 ± .223 (95)	.468 ± .202 (106)	.829 ± .246 (93)	2.798 ± .880 (100)	.424 ± .111 (102)
Sodium	.075 ± .022 (66)	.089 ± .030 (151)	.103 ± .033 (39)	.236 ± .083 (54)	.284 ± .094 (72)	.166 ± .057 (86)	.498 ± .199 (74)	.961 ± .260 (70)	.100 ± .031 (67)
Potassium	.007 ± .004 (66)	.009 ± .004 (152)	.015 ± .005 (39)	.024 ± .006 (55)	.038 ± .010 (72)	.035 ± .011 (86)	.063 ± .019 (74)	.074 ± .019 (69)	.023 ± .010 (67)
Ammonium	.007 ± .006 (47)	.004 ± .004 (4)	.002 ± .002 (25)	—— (0)	.008 ± .005 (47)	.007 ± .007 (51)	.007 ± .007 (46)	.009 ± .012 (46)	.010 ± .010 (46)
Sulfate	.207 ± .037 (108)	.163 ± .032 (152)	.188 ± .038 (49)	.285 ± .048 (55)	.633 ± .154 (105)	.460 ± .107 (111)	.968 ± .232 (106)	5.651 ± 2.673 (107)	.281 ± .088 (107)
Nitrate	.023 ± .016 (47)	.017 ± .011 (95)	.011 ± .007 (52)	.038 ± .012 (54)	.052 ± .030 (47)	.047 ± .017 (52)	.551 ± .211 (47)	.077 ± .049 (46)	.020 ± .014 (46)
Chloride	.057 ± .032 (113)	.090 ± .042 (152)	.076 ± .032 (54)	.276 ± .138 (55)	.329 ± .112 (109)	.174 ± .058 (117)	.044 ± .035 (47)	1.301 ± .275 (112)	.064 ± .032 (114)
Bicarbonate	.166 ± .065 (115)	.222 ± .078 (136)	.357 ± .205 (52)	1.219 ± .638 (55)	1.525 ± .634 (109)	1.599 ± .584 (120)	2.241 ± .461 (107)	3.915 ± .801 (116)	.098 ± .209 (117)
Phosphate	.001 ± .001 (83)	.001 ± .001 (132)	.001 ± .001 (22)	—— (1)	.006 ± .012 (82)	.004 ± .003 (84)	.003 ± .004 (82)	.004 ± .003 (82)	.006 ± .004 (82)

Table 8.—Results of linear, hyperbolic, and general hyperbolic relationships between chemical concentration and discharge of surface water at all stations

[All relationships are in the form $C_i = A \cdot f(Q) + b$, where Y is concentration and $f(Q)$ is equal to X, linear; $1/X$, hyperbolic; and $1/(1 + {}_b \cdot X)$, general hyperbolic. R^2 is coefficient of determination. Number of observations is in parentheses. Locations are given in fig. 1]

f(Q)	Hydrogen				Calcium				Ammonium			
	a	b	β	100R^2	a	b	β	100R^2	a	b	β	100R^2
East Branch Sacandaga River at Griffin:												
Linear	21.2×10^{-9}	0.163	(115)	[3]21.7	-0.53×10^{-5}	0.28	(101)	[3]28.1	0.6×10^{-6}	0.0057	(47)	3.3
Hyperbolic	−21.64	.252		[3]10.3	9.28	.25		[3]37.7	.302	.0060		1.0
General hyperbolic	-7.4×10^{-4}	8.6×10^{-4}	$10^{-4.0}$	[3]32.0	.16	.22	$10^{-2.5}$	[3]61.4	−.1844	.1900	$10^{-5.5}$	3.1
Esopus Creek at Shandaken:												
Linear	14.2×10^{-9}	.240	(152)	.5	-1.3×10^{-5}	.30	(151)	[3]26.9	----	----	----	----
Hyperbolic	−27.26	.318		2.0	14.69	.24		[3]37.9	----	----	----	----
General hyperbolic	-3.8×10^{-4}	3.7×10^{-4}	$10^{-2.5}$	[2]2.9	.18	.19	$10^{-3.0}$	[3]52.5	----	----	----	----
Oquaga Creek near North Sanford:												
Linear	3.9×10^{-9}	.317	(67)	0	-6.8×10^{-5}	.44	(39)	[3]41.2	$-.0 \times 10^{-6}$	.0013	(35)	.0
Hyperbolic	1.09	.314		0	9.64	.23		[3]57.7	−.157	.0017		2.9
General hyperbolic	-2.7×10^{-4}	3.8×10^{-4}	$10^{-2.0}$	1.2	.40	.20	$10^{-2.5}$	[3]65.7	.066	−.064	$10^{-5.5}$	.9
Gridley Creek above East Virgil:												
Linear	4.4×10^{-9}	.051	(55)	4.5	-11.8×10^{-5}	1.45	(55)	[3]37.5	----	----	----	----
Hyperbolic	−6.71	.073		[1]6.5	218.65	.78		[3]78.6	----	----	----	----
General hyperbolic	$-.85 \times 10^{-4}$	1.2×10^{-4}	$10^{-3.5}$	[2]9.4	2.46	.47	$10^{-2.5}$	[3]93.1	----	----	----	----
Fivemile Creek near Kanona:												
Linear	8.3×10^{-9}	.016	(109)	[3]59.3	-11.42×10^{-5}	1.79	(95)	[3]33.7	$.6 \times 10^{-6}$	.0066	(47)	[3]17.7
Hyperbolic	−.70	.031		[2]10.2	23.22	1.47		[3]31.9	−.012	.0076		.1
General hyperbolic	-5.5×10^{-4}	5.7×10^{-4}	$10^{-5.5}$	[3]60.1	1.74	.72	$10^{-3.5}$	[3]86.1	−.044	.051	$10^{-5.5}$	[3]17.6
Conewango Creek at Waterboro:												
Linear	8.5×10^{-9}	.032	(120)	[3]33.2	-19.93×10^{-5}	1.98	(106)	[3]64.8	1.5×10^{-6}	.0051	(51)	[2]10.9
Hyperbolic	−6.41	.058		[3]17.1	221.85	1.23		[3]63.0	−.317	.0080		.9
General hyperbolic	-9.1×10^{-4}	9.4×10^{-4}	$10^{-5.0}$	[3]33.2	1.97	.64	$10^{-4.0}$	[3]84.9	−.055	.060	$10^{-4.5}$	[2]11.1
Buffalo Creek at Gardenville:												
Linear	2.9×10^{-9}	.013	(105)	[3]22.8	-11.40×10^{-5}	2.57	(91)	[3]14.1	1.5×10^{-6}	.0045	(46)	[3]35.7
Hyperbolic	−.54	.019		[1]3.3	−10.34	2.48		1.0	−.248	.0076		1.5
General hyperbolic	-9.4×10^{-4}	9.5×10^{-4}	$10^{-5.5}$	[3]22.7	11.9	9.37	$10^{-5.0}$	[3]13.9	−.48	.49	$10^{-5.5}$	[3]35.6
Black Creek at Churchville:												
Linear	$.9 \times 10^{-9}$	.013	(116)	1.9	-106.68×10^{-5}	8.81	(100)	[3]52.3	$-.5 \times 10^{-6}$	.010	(46)	.8
Hyperbolic	−.04	.014		.4	60.91	7.37		[3]15.1	.426	.0080		1.9
General hyperbolic	$-.14 \times 10^{-4}$	$.27 \times 10^{-4}$	$10^{-4.0}$	2.1	7.38	3.00	$10^{-3.0}$	[3]69.6	.0095	.0058	$10^{-2.5}$	4.4
Deer River at Brasher Iron Works:												
Linear	2.0×10^{-9}	.043	(115)	1.3	-2.03×10^{-5}	.87	(100)	[3]7.8	$-.1 \times 10^{-6}$	.011	(46)	.0
Hyperbolic	−2.69	.050		[1]3.1	10.47	.82		.5	−.144	.011		.2
General hyperbolic	$-.37 \times 10^{-4}$	$.65 \times 10^{-4}$	$10^{-3.0}$	[2]4.3	.45	.43	$10^{-4.0}$	[3]9.4	.0054	.0077	$10^{-3.0}$	1.4

Table 8.—Results of linear, hyperbolic, and general hyperbolic relationships between chemical concentration and discharge of surface water at all stations—Continued

f(Q)	Nitrate				Sulfate				Chloride			
	a	*b*	β	100R^2	*a*	*b*	β	100R^2	*a*	*b*	β	100R^2
East Branch Sacandaga River at Griffin:												
Linear	3.3×10^{-6}	.017	(47)	[3]16.2	-1.6×10^{-6}	0.21	(108)	[1]3.3	-2.1×10^{-6}	0.062	(112)	[3]7.0
Hyperbolic	−3.68	.029		[3]22.7	−2.22	.21		[1]2.8	3.91	.049		[3]11.1
General hyperbolic	−.048	.037	$10^{-2.5}$	[3]31.4	.047	.17	$10^{-4.0}$	[1]3.4	.064	.024	$10^{-3.0}$	[3]70.8
Esopus Creek at Shandaken:												
Linear	3.2×10^{-6}	.011	(95)	[3]25.3	$.8 \times 10^{-6}$	.16	(151)	.3	-6.2×10^{-6}	.10	(150)	[3]11.0
Hyperbolic	−1.77	.020		[3]11.7	−.95	.16		.4	7.69	.078		[3]19.0
General hyperbolic	−.050	.060	$10^{-4.0}$	[3]25.5	−.25	.41	$10^{-5.5}$	.3	.099	.065	$10^{-2.5}$	[3]23.1
Oquaga Creek near North Sanford:												
Linear	-1.2×10^{-6}	.012	(62)	4.7	2.9×10^{-6}	.18	(56)	1.1	1.9×10^{-6}	.076	(64)	.7
Hyperbolic	1.74	.0074		[3]25.2	−1.97	.19		1.3	−.62	.074		.2
General hyperbolic	.0070	.0065	$10^{-3.0}$	[1]5.5	.024	.18	$10^{-2.0}$	4.6	.0150	.073	$10^{-2.0}$	1.6
Gridley Creek above East Virgil:												
Linear	$-.3 \times 10^{-6}$	.038	(54)	.5	-7.3×10^{-6}	.30	(55)	[3]18.4	-25.7×10^{-6}	.326	(55)	[3]27.8
Hyperbolic	−1.33	.040		4.0	11.40	.26		[3]27.3	39.33	.197		[3]39.4
General hyperbolic	−.019	.040	$10^{-5.5}$	3.3	.11	.23	$10^{-3.0}$	[3]32.5	.39	.073	$10^{-3.0}$	[3]50.7
Fivemile Creek near Kanona:												
Linear	$.2 \times 10^{-6}$	.052	(47)	.0	-24.5×10^{-6}	.66	(105)	[3]16.6	-24.0×10^{-6}	.36	(109)	[3]29.0
Hyperbolic	−1.18	.061		[3]24.0	.42	.63		.1	3.95	.30		[3]18.5
General hyperbolic	−.080	.067	$10^{-2.5}$	[3]29.6	.83	−.15	$10^{-5.0}$	[3]20.2	.42	.027	$10^{-4.0}$	[3]70.8
Conewango Creek at Waterboro:												
Linear	-1.8×10^{-6}	.050	(52)	4.9	-29.9×10^{-6}	.51	(111)	[3]31.7	-14.2×10^{-6}	.20	(117)	[3]23.6
Hyperbolic	−2.38	.052		[2]8.7	33.79	.40		[3]34.8	14.66	.15		[3]22.5
General hyperbolic	−.034	.052	$10^{-2.0}$	[1]6.6	.29	.32	$10^{-3.0}$	[3]41.7	.13	.11	$10^{-3.0}$	[3]27.0
Buffalo Creek at Gardenville:												
Linear	5.7×10^{-6}	.034	(47)	[3]18.1	-33.2×10^{-6}	1.00	(104)	[3]8.8	-3.2×10^{-6}	.55	(105)	.1
Hyperbolic	−8.58	.070		[3]62.7	7.93	.094		[3]2.1	−6.66	.57		1.9
General hyperbolic	−.17	.078	$10^{-2.0}$	[3]67.8	.69	.34	$10^{-4.0}$	[3]10.8	−.18	.58	$10^{-2.0}$	2.3
Black Creek at Churchville:												
Linear	3.3×10^{-6}	.073	(46)	1.7	$-1{,}163.2 \times 10^{-6}$	6.93	(107)	[3]42.7	-127.9×10^{-6}	1.44	(112)	[3]47.3
Hyperbolic	−6.36	.099		[3]23.8	101.3	5.12		[3]25.6	4.87	1.28		[3]5.4
General hyperbolic	−.14	.107	$10^{-2.0}$	[3]26.7	9.04	1.94	$10^{-2.5}$	[3]75.6	1.12	.40	$10^{-3.5}$	[3]51.2
Deer River at Brasher Iron Works:												
Linear	$.6 \times 10^{-6}$	.019	(46)	1.5	5.7×10^{-6}	.29	(105)	1.9	-3.5×10^{-6}	.069	(112)	[2]5.0
Hyperbolic	.09	.020		.0	−1.00	.28		.1	2.14	.060		2.2
General hyperbolic	−.014	.030	$10^{-3.5}$	3.4	.25	.036	$10^{-4.5}$	2.1	.047	.039	$10^{-3.5}$	[3]8.1

Table 8.—Results of linear, hyperbolic, and general hyperbolic relationships between chemical concentration and discharge of surface water at all stations—Continued

$f(Q)$	Alkalinity				Specific conductance				Total ions			
	a	b	β	$100R^2$	a	b	β	$100R^2$	a	b	β	$100R^2$
East Branch Sacandaga River at Griffin:												
Linear	-0.4×10^{-3}	9.0	(115)	[3]20.3	−0.0010	49.2	(115)	[3]28.2	-0.20×10^{-4}	0.91	(65)	[3]34.9
Hyperbolic	875.5	6.4		[3]54.3	1,554.4	43.8		[3]28.3	33.73	.78		[3]38.1
General hyperbolic	13.8	4.0	$10^{-2.5}$	[3]77.7	26.0	33.4	$10^{-3.0}$	[3]60.8	.609	.54	$10^{-3.0}$	[3]83.3
Esopus Creek at Shandaken:												
Linear	$-.8\times10^{-4}$	12.9	(150)	[3]25.2	−.0023	58.3	(152)	[3]31.0	$-.47\times10^{-4}$	1.05	(132)	[3]34.0
Hyperbolic	860.4	9.6		[3]31.1	2,563.0	49.0		[3]43.9	50.39	.86		[3]43.9
General hyperbolic	10.4	6.4	$10^{-3.0}$	[3]44.5	34.8	44.4	$10^{-2.5}$	[3]59.1	.632	.66	$10^{-3.0}$	[3]65.2
Oquaga Creek near North Sanford:												
Linear	-4.8×10^{-3}	23.3	(66)	[3]42.3	−.0095	79.0	(67)	[3]41.9	-1.99×10^{-4}	1.49	(32)	[3]42.2
Hyperbolic	3,456.0	8.0		[3]68.7	6,951.7	48.6		[3]63.2	126.18	.90		[3]60.6
General hyperbolic	31.7	5.1	$10^{-2.5}$	[3]76.8	62.0	43.2	$10^{-2.5}$	[3]71.7	1.21	.77	$10^{-2.5}$	[3]79.4
Gridley Creek above East Virgil:												
Linear	-7.0×10^{-3}	74.6	(55)	[3]38.9	−.0175	231.	(55)	[3]44.4	-3.47×10^{-4}	4.31	(54)	[3]41.2
Hyperbolic	12,740.4	35.5		[3]77.5	28,756.3	139.		[3]73.1	613.18	2.41		[3]78.8
General hyperbolic	145.2	16.8	$10^{-2.5}$	[3]94.5	289.0	43.4	$10^{-3.0}$	[3]94.5	6.956	1.53	$10^{-2.5}$	[3]94.3
Fivemile Creek near Kanona:												
Linear	-6.5×10^{-3}	84.6	(109)	[3]25.4	−.0175	282.	(109)	[3]33.8	-3.29×10^{-4}	5.49	(72)	[3]34.5
Hyperbolic	1,793.4	64.0		[3]45.8	3,353.3	237.		[3]29.2	73.00	4.43		[3]36.8
General hyperbolic	111.4	17.4	$10^{-3.5}$	[3]91.5	301.7	43.0	$10^{-4.0}$	[3]81.7	5.96	1.18	$10^{-3.0}$	[3]91.9
Conewango Creek at Waterboro:												
Linear	-12.0×10^{-3}	101.6	(120)	[3]65.0	−.0273	280.	(120)	[3]62.7	-5.40×10^{-4}	5.54	(86)	[3]67.5
Hyperbolic	13,111.0	57.2		[3]69.8	29,075.1	180.		[3]64.0	636.18	3.42		[3]67.8
General hyperbolic	117.8	22.0	$10^{-3.0}$	[3]91.2	260.	103.	$10^{-3.0}$	[3]82.5	5.71	1.74	$10^{-3.0}$	[3]91.3
Buffalo Creek at Gardenville:												
Linear	-6.8×10^{-3}	121.5	(105)	[3]36.2	−.0149	396.	(105)	[3]20.6	-4.96×10^{-4}	8.11	(72)	[3]32.7
Hyperbolic	1,429.2	107.8		[3]6.6	2,024.5	370.		1.6	55.69	7.31		2.6
General hyperbolic	140.7	−14.6	$10^{-4.0}$	[3]43.7	303.2	102.	$10^{-4.0}$	[3]23.9	52.4	−44.26	$10^{-5.0}$	[3]32.8
Black Creek at Churchville:												
Linear	-5.9×10^{-3}	202.3	(116)	[2]4.7	−.1326	1160.	(116)	[3]58.9	-26.43×10^{4}	24.93	(69)	[3]65.3
Hyperbolic	1,173.4	202.7		[3]15.0	6,952.4	982.		[3]13.2	136.60	20.96		[3]15.3
General hyperbolic	−79.5	215.4	$10^{-2.0}$	[3]17.3	1,222.	33.9	$10^{-3.5}$	[3]71.3	26.08	1.14	$10^{-3.5}$	[3]80.1
Deer River at Brasher Iron Works:												
Linear	-1.8×10^{-3}	51.5	(115)	[3]11.7	−.0048	139.	(115)	[3]15.1	$-.93\times10^{-4}$	2.89	(65)	[3]17.4
Hyperbolic	878.6	47.5		[2]3.5	2,356.8	128.		[2]4.2	110.55	2.56		[1]5.5
General hyperbolic	25.7	28.8	$10^{-3.5}$	[3]16.4	66.7	81.7	$10^{-4.0}$	[3]18.8	2.208	.80	$10^{-4.0}$	[3]22.8

[1] Indicates statistical significance $\alpha<0.10$.
[2] Indicates statistical significance $\alpha<0.05$.
[3] Indicates statistical significance $\alpha<0.01$.

Table 9.—Results of best temporal-trend analysis of residual surface-water data by nonparametric seasonal Kendall test

[*f*(*Q*) refers to relationship between constituent concentration and stream discharge (table 8), where M = mean, L = linear, H = hyperbolic, and G = general hyperbolic. Where no significant relationship exists, predicted constituent concentration is equal to its mean. Average percent slope (trends per year is calculated by dividing slope by the mean concentration in table 7. Location is given in fig. 1]

Station	Hydrogen			Calcium			Ammonium			Nitrate		
	Slope	Average percent slope	*f*(*Q*)	Slope	Average percent slope	*f*(*Q*)	Slope	Average percent slope	*f*(*Q*)	Slope	Average percent slope	*f*(*Q*)
East Branch Sacandaga River at Griffin	-----	-----	--	-----	-----	--	−0.0012	[1]−2.0	G	0.0040	[3]17.5	G
Esopus Creek at Shandaken	-----	-----	--	-----	-----	--	-----	-----	--	-----	-----	--
Oquaga Creek near North Sanford	26.4×10^{-6}	[3]8.1	M	-----	-----	--	-----	-----	--	.0009	[2]8.4	H
Gridley Creek above East Virgil	-----	-----	--	-----	-----	--	-----	-----	--	−.0018	[2]−4.9	M
Fivemile Creek near Kanona	1.0×10^{-6}	[2]3.8	G	-----	-----	--	-----	-----	--	− .0054	[1]−10.4	G
Conewango Creek at Waterboro	-----	-----	--	0.0194	[3]1.2	G	-----	-----	--	-----	-----	--
Buffalo Creek at at Gardenville	$-.8 \times 10^{-6}$	[3]−5.9	L	-----	-----	--	-----	-----	--	.0051	[1]11.8	G
Black Creek at Churchville	-----	-----	--	−.1066	[2]−1.4	G	-----	-----	--	-----	-----	--
Deer River at Brasher Iron Works	-3.5×10^{-6}	[3]−8.0	G	-----	-----	--	-----	-----	--	-----	-----	--

Station	Sulfate			Chloride			Total Ions			Specific Conductance			Alkalinity		
	Slope	Average percent slope	*f*(*Q*)	Slope	Average percent slope	*f*(*Q*)	Slope	Average percent slope	*f*(*Q*)	Slope	Average percent slope	*f*(*Q*)	Slope	Average percent slope	*f*(*Q*)
East Branch Sacandaga River at Griffin	−0.0041	[3]−2.0	G	0.0011	[1]2.0	G	−0.0110	[1]−1.3	G	-----	-----	--	−0.083	[2]−1.0	G
Esopus Creek at Shandaken	−.0035	[3]−2.1	M	-----	-----	--	-----	-----	--	-----	-----	--	.098	[1].9	G
Oquaga Creek near North Sanford	-----	-----	--	-----	-----	--	-----	-----	--	−.5	[1]−.8	G	-----	-----	--
Gridley Creek above East Virgil	-----	-----	--	.0171	[3]7.3	G	-----	-----	--	-----	-----	--	2.072	[2]3.4	G
Fivemile Creek near Kanona	−.0100	[2]−1.6	G	-----	-----	--	-----	-----	--	3.2	[3]1.2	G	1.285	[3]1.6	G
Conewango Creek at Waterboro	−.0048	[2]−1.0	G	.0118	[3]6.8	G	.0475	[3]1.1	G	4.6	[3]2.0	G	-----	-----	--
Buffalo Creek at at Gardenville	−.0172	[3]−1.8	G	.0141	[3]2.6	M	-----	-----	--	-----	-----	--	-----	-----	--
Black Creek at Churchville	−.0776	[2]−1.4	G	-----	-----	--	−.2794	[2]−1.3	G	-----	-----	--	-----	-----	--
Deer River at Brasher Iron Works	−.0104	[3]−3.7	M	.0034	[3]5.2	G	-----	-----	--	-----	-----	--	-----	-----	--

[1] Indicates statistical significance $\alpha < 0.10$.
[2] Indicates statistical significance $\alpha < 0.05$.
[3] Indicates statistical significance $\alpha < 0.01$.

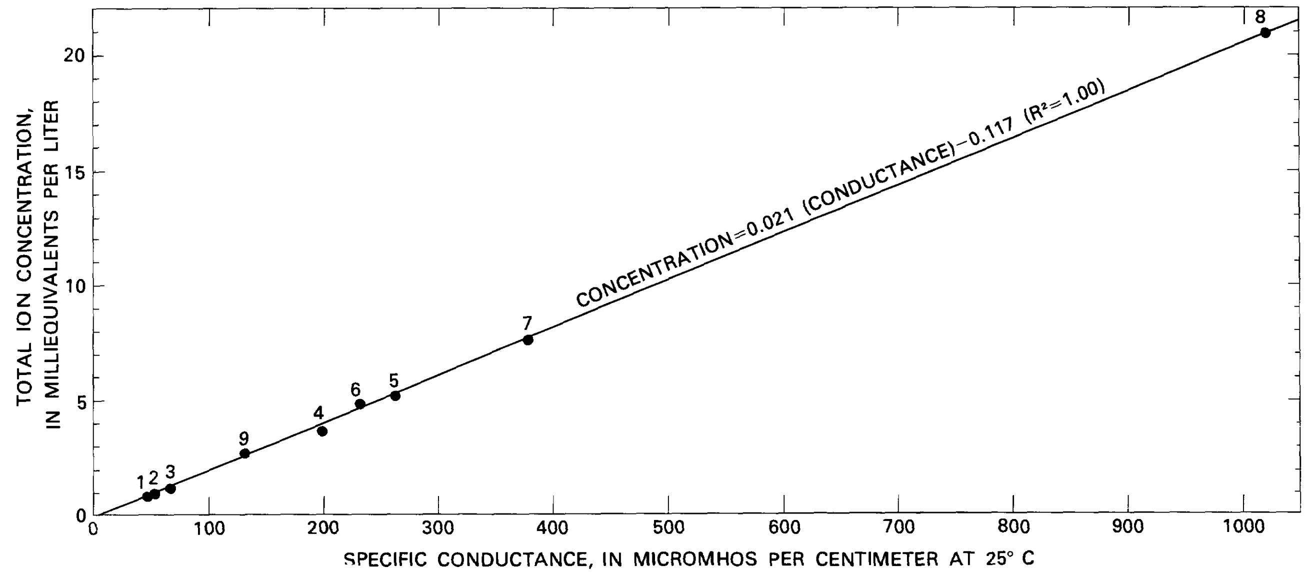

Figure 10.—Relationship between mean total ion concentration and specific conductance at all surface-water stations (numbers next to data points correspond to stations in fig.1).

SUMMARY

Chemical composition of precipitation in New York is affected by local as well as regional influences. Although the entire State has reportedly been subject to "acid precipitation" for 30 to 50 years, the concentration of free hydrogen ion has changed little on a Statewide basis for the 13-year period beginning in 1965. In the western part of the State, however, hydrogen-ion concentration seems to have increased by about 3 percent annually since 1965, equivalent to a total decrease of 0.2 pH units. In the eastern part of the State, hydrogen-ion concentration has decreased by a comparable amount. The hydrogen-ion load within the western and central parts of the State has increased slightly in recent years because precipitation quantity there has increased by an average of 2 to 3 percent annually since 1965.

Trends of sulfate, an acid-forming anion, are more easily discerned than those of hydrogen. Sulfate concentration has decreased an average of 1 to 4 percent per year. Trends in nitrate concentration were not detected at most stations. Trends in pH cannot be predicted simply from trends in these acid-forming anions, however, because dryfall contributes neutralizing material to precipitation and because chemical composition of dryfall may also change with time.

Although statistically significant trends in pH of surface water are indicated in some other areas of the State, the impact from precipitation is masked by the greater effects of agriculture and urbanization. However, Statewide decreases in sulfate concentrations in streams were detected and averaged 1 to 4 percent per year. These decreases were similar to those detected in precipitation.

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Conversion Factors and Abbreviations

The following factors may be used for converting the International System (SI) units of measure used in this report to inch-pound units:

Multiply SI units	*By*	*To obtain inch-pound units*
Length		
centimeter (cm)	2.54	inch (in.)
meter (m)	.3048	foot (ft)
kilometer (km)	.6214	mile (mi)
Area		
square kilometer (km^2)	.3861	square mile (mi^2)
Flow		
cubic meters per second (m^3/s)	35.31	cubic feet per second (ft^3/s)
cubic meters per day per square kilometer ((m^3/d)/km^2)	91.49	cubic feet per day per square mile [(ft^3/d)/mi^2]

Other abbreviations used in this report:
meq/L, milliequivalents per liter;
μeq, microequivalents;
(meq/L)/yr, milliequivalents per liter per year;
(μeq/L)/yr, microequivalents per liter per year;
μmho/cm at 25° C, micromhos per centimeter at 25° Celsius;
cm/yr, centimeters per year;
$km^2 \cdot d/m^3$, square kilometer-day per cubic meter;
(μmho/cm)/eq, micromhos per centimeter per equivalent.

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