

# An Evaluation of Trends in the Acidity of Precipitation and the Related Acidification of Surface Water in North America

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# An Evaluation of Trends in the Acidity of Precipitation and the Related Acidification of Surface Water in North America

By JOHN T. TURK

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# An Evaluation of Trends in the Acidity of Precipitation and the Related Acidification of Surface Water in North America

By John T. Turk

## Abstract

The acidity of precipitation in the Northeastern United States and Southeastern Canada has increased in the past, probably as a result of anthropogenic emissions. The increase in New England and New York occurred primarily before the mid-1950's. Since the mid-1960's, there has been no significant change in the acidity of precipitation in this region; however, sulfate concentrations have decreased and nitrate concentrations may have increased. The time of initial acidification in Southeastern Canada is not known because of a lack of historical data. In the Southeastern United States, the evaluation of whether precipitation has been acidified is complicated by meager data. The available data show that precipitation is more acidic than would be expected for sites unaffected by anthropogenic emissions. In addition, comparison of recent data with the meager historical data suggests, but does not unambiguously prove, increased acidification since the 1950's. In the Western United States, available data indicate that precipitation at individual sites has been acidified by anthropogenic emissions. The acidification generally has been attributable to localized sources, and the time of initial acidification is undefined.

Acidification of lakes and streams in the Northeastern United States has occurred in a time frame compatible with the hypothesis that acidification of precipitation was the cause. The acidification of surface waters appears to have occurred before the mid- to late 1960's. In Southeastern Canada, the best-documented cases of acidified lakes point to localized sources of acidic emissions as the cause. Sparse evidence of recent regional acidification of lakes and streams exists, but evidence for acidification of precipitation as the cause is largely lacking. In the Southeastern United States, most data on acidification of surface waters are ambiguous, and in the West, most of the data reflect local conditions. However, recent analysis of a national network of remote stream sampling stations indicates that, since the mid- to late 1960's, sulfate concentrations have increased in the Southeast and the West, with a concurrent decrease in alkalinity. Additional work is needed to test the hypothesis that regional acidification of surface waters is occurring in the Southeastern and Western United States.

## INTRODUCTION

Anthropogenic, or "man-caused," acid rain is a concept that has been used to explain changes in the chemistry and biology of dilute aquatic systems in North America and northern Europe. The concept has developed over more than 100 years, first in Europe and later in North America. The historical and geographic evolution of this concept is documented in the technical literature on atmospheric chemistry, aquatic chemistry, fisheries, soils, forestry, and agriculture. An excellent summary of this evolution is given by Cowling (1982).

The regional and international nature of the acid-rain concept requires an understanding of the acidification process both in precipitation and in susceptible aquatic systems. Without an adequate understanding of the relation of the acidification process to time trends and controlling mechanisms, corrective measures cannot be developed to provide effective long-term or short-term solutions. Trend analysis can be used as a first step in the determination of important sources, transformations, and impacts of acid rain.

Trend analysis is a useful tool in many aspects of the scientific, political, and economic consideration of acid rain and its effects. Among the issues that can be addressed by trend analysis are:

1. The development of cost-effective control or mitigative procedures will require an evaluation of the importance of natural and anthropogenic sources of acidity. Similar trends in supposed sources and in impacts on precipitation or aquatic systems can serve as an aid in deciding which sources are most directly related to the impacts. Such initial decisions can provide direction to more detailed study to prove or disprove proposed relations between changes in emissions and impacts.
2. A documentation of the extent and value of damages caused by acid rain is necessary for both mitigation and assignment of legal responsibility. Trend analysis can be used to determine which geographic areas have been damaged and to assess the damage in ecologic or economic terms.

3. Definition of the watershed characteristics and processes that are most affected by acid rain, particularly with respect to the order in which changes occur, is necessary to provide the scientific understanding of how acid rain causes the changes ascribed to it. Trend analysis should be most useful in this aspect of problem definition.

The numerous uses of trend analysis with respect to acid rain have resulted in exhaustive searches for data bases which might allow trend detection. Unfortunately, the collection of data in past studies has resulted in data bases that normally do not meet all the needs of a trend analysis. Because investigators in previous studies did not know the uses to which their data would be applied, crucial measurements often were not made. Similarly, documentation of methodology and quality control are lacking. In comparing older data with recent data, changes in analytical methodology further complicate trend detection. As a result, the capability of trend analyses to show trends has varied among geographic areas, individual chemical constituents, and data bases. Further, reports generally have been quite limited in the geographic area covered by the investigator. Most studies have been local or statewide, and only a few have been regional in scope. Only one study, limited to surface waters, has been conducted on a nationwide scale (Smith and Alexander, 1983).

## Purpose and Scope

This report is intended to critically evaluate published trend information about the chemical quality of precipitation and of dilute surface waters that may have been significantly affected by changes in precipitation quality. The results of several studies within individual geographic regions were combined to assess whether changes in chemical quality have occurred. To the extent that the available data permit, several hypotheses on why trends are or are not found are evaluated. It is beyond the scope of this study, however, to provide new data or new trend analyses of data used in previous publications.

In addition to evaluating whether trends in acidification have occurred, this report assesses the certainty of assigning time periods for the initiation of reported changes. While it may seem trivial whether an area became acidified in the last 10, 50, or 100 years, this is not the case. Our understanding of the response of precipitation to changes in atmospheric emissions, at least in terms of long-term average responses, is seriously hampered by the uncertainty in estimating rates of change in acidification in specific regions. If historical data are inadequate to address this question, then estimates of response must be made on assumptions untested for long-term validity, or must be postponed until an adequate data base can be developed. In the application of expensive

mitigative or preventive measures to serious environmental problems, neither alternative is desirable.

## Acknowledgments

This study was greatly assisted by the cooperation of researchers who provided information on applicable publications and made available copies of their work, often before they were printed. Denise Wiltshire, of the U.S. Geological Survey in Albany, N. Y., provided an invaluable contribution with a streamlined bibliographic search, preliminary review of content, and retrieval. Owen Bricker, Robert Hirsch, Douglas Manigold, and David Rickert of the Geological Survey provided numerous improvements to the manuscript.

## APPROACH

### Literature Search

Reviewing the literature on trends in the acidity of precipitation and surface water entailed: (1) conducting computerized bibliographic searches of the data bases listed in table 1; (2) searching published bibliographies of

**Table 1.** Description of data bases searched

Name of data base	Time coverage of data base	Description
Aqualine	1974 to present	Indexing data base of the Water Research Center, Buckinghamshire, England
CA Search	1967 to present	Online version of Chemical Abstracts
Enviroline	1970 to present	Bibliographic data base for environmental energy information produced by Environment Information Center, N.Y.
GEOREF	1961 to present	Earth-sciences data base produced by American Geological Institute, Falls Church, Va.
NTIS	1964 to present	Data base of government-sponsored research reports produced by National Technical Information Service, Springfield, Va.
Pollution Abstracts	1970 to present	Online version of Pollution Abstracts
Selected Water-Resources Abstracts	1968 to present	Online version of Selected Water-Resources Abstracts

Rambo and Karanas (1982), Dailey and Winslow (1980), and Wiltshire and Evans (1983); and (3) communicating with scientists researching acid precipitation.

Keywords used in searching the computerized bibliographies are listed in table 2. Keywords were selected from the "Water Resources Thesaurus" (U.S. Office of Water Research and Technology, 1980), "GEOREF Thesaurus and Guide to Indexing" (Riley, 1981), and "Enviroline User's Manual, appendix F", Keyword Lists (Environment Information Center, 1982).

Results of the computerized and manual literature searches were reviewed. Retrieved documents were assessed for relevance to the scope of investigation and evaluated for problems that could influence the reliability of the conclusions.

## Evaluation of Trend Data

Although the purpose of this work is to develop a continental-scale evaluation of trends in the acidification of precipitation and changes in surface-water chemistry that can be attributed to acid rain, it is useful to consider separately the published information by geographic area and by type of data (precipitation or surface water). The usefulness of this approach is that changes in anthropogenic emissions to the atmosphere have not occurred uniformly in time, in chemical composition, or in magnitude for all sections of North America. Further, the prevailing westerly movement of weather systems across the United States tends to cause certain clusters of emissions sources to affect the precipitation quality in regions that are somewhat stratified by latitude (fig. 1). For example, emissions in the Northeastern United States often influence the quality of precipitation in that part of the Nation, and only infrequently affect the quality in the Southeastern United States. Because the scatter in chemical-concentration data is often related to the concentration, very dilute water such as precipitation may exhibit a significant

trend but more concentrated surface-water data may not, even though both have trends of the same magnitude. Thus, it is useful to consider the trend information for precipitation separately from that for surface water. Unavailability of trend data from Mexico and much of Canada makes analysis on a continental scale difficult.

In addition to the usefulness of considering geographic area, precipitation, and surface water as class variables and thereby restricting the investigation to these classes, some consideration also must be given to what actually constitutes a significant trend. In the simplest sense, a time trend can be defined as a statistically significant difference in some variable—alkalinity, sulfate, nitrate, or pH—between two time periods. In such a case, a set of measurements of the variable of interest, with sufficient information on random and systematic errors affecting measurements in both time periods, is the only information necessary to determine whether a trend has occurred. Unfortunately, these ancillary data are commonly not available. In these instances, some estimate of the range of measurement error and bias must be applied to judge the likelihood of a trend actually existing.

Many of the sources of error inherent in the simple comparison of the mean value of a variable in two separate time periods can be estimated or minimized if a continuous data set is available rather than a separate, short-term set for two separate time periods. Errors caused by seasonality, changes in analytical methodology, climatic variability, and other sources can be addressed more adequately in a continuous data set. Unfortunately, such data bases tend to be much less commonly reported than mean values.

Given that the most appropriate data sets are not routinely available for the class variables considered, some mix of mean value and continuous data is necessary to perform an analysis for trends. The approach used in this report is to consider the sources of error that can be approximated and to examine the consistencies or inconsistencies of the trends among the data sets available. As a contribution to future work of this type, some suggestions for improvements in data collection are given.

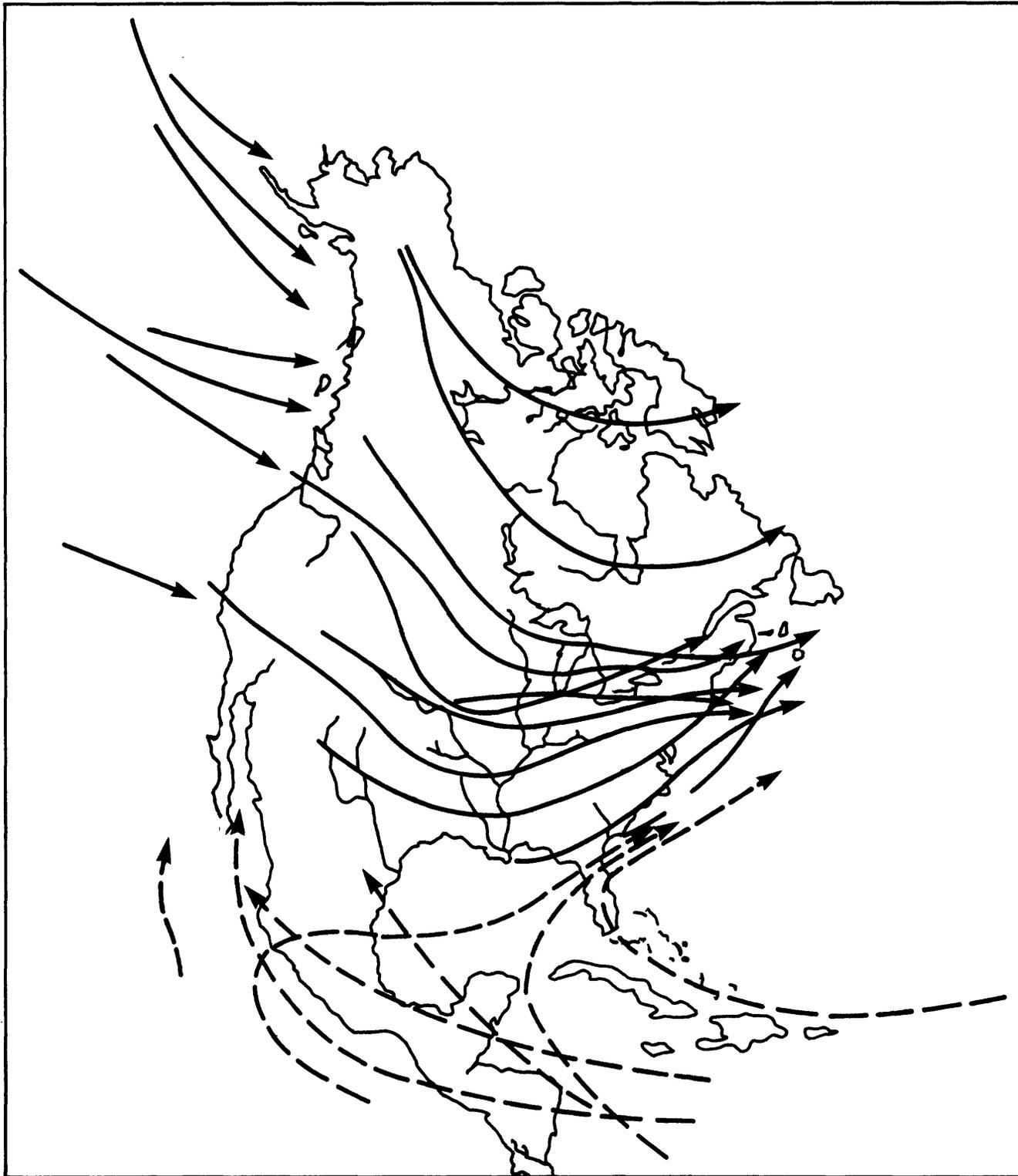
Table 2. Keywords used in bibliographic searches

Terms related to precipitation chemistry	Terms related to trend analysis
Acid rain	Trend(s)
Acid precipitation	Temporal distribution
Acidic deposition	Spatial distribution
Acidic water	History
Sulfate, sulfates	
Nitrate, nitrates	
Hydrogen-ion concentration	

## RESULTS

### pH of Natural Precipitation

The pH of natural precipitation is of great importance in detecting trends in acidity where reliable historical data are not available. Early work assumed a natural pH of about 5.6 (Likens, 1976), the pH of pure water in equilibrium with atmospheric carbon dioxide. While acidification relative to some presumed fixed level of acidity would seem an easy calculation, data indicate that a range of pH from about 4.5 to 5.6, rather than a fixed



**Figure 1.** Major climatological storm tracks for the North American continent. (Adapted from Haurwitz and Austin, 1944).

value of 5.6, should be expected in precipitation in the absence of significant anthropogenic acidification. This range of pH values is derived from consideration of the natural sulfur, nitrogen, and water cycles (Charlson and Rodhe, 1982). Indeed, the average pH of precipitation in locations remote from local anthropogenic acidification sources has been shown to be 4.8 to 5.0 (Galloway and others, 1982), although some part of this acidity is probably due to long-range transport from more developed areas. Galloway and others (1982) state the "...lower limit of the natural mean pH was probably  $\geq 5$ ." A significant part of the natural acidity probably was contributed by formic and acetic acids which were shown to be important in some of the samples. Thus, acidification should not be presumed as an excess of hydrogen ion relative to arbitrary, calculated pH values based on oversimplifying assumptions such as equilibration with atmospheric carbon dioxide as the only natural acidification control. The natural pH is probably a very site-specific value, with its magnitude at a site subject to natural temporal variation. Values of pH will be a function of at least global and local climate, additions of weak and strong acids, and additions of alkaline ions and compounds—the additions being contributed now by both natural and anthropogenic processes.

## **Midwestern-Northeastern United States and Southeastern Canada**

### **Synoptic Data Indicating Trends in Precipitation Acidification**

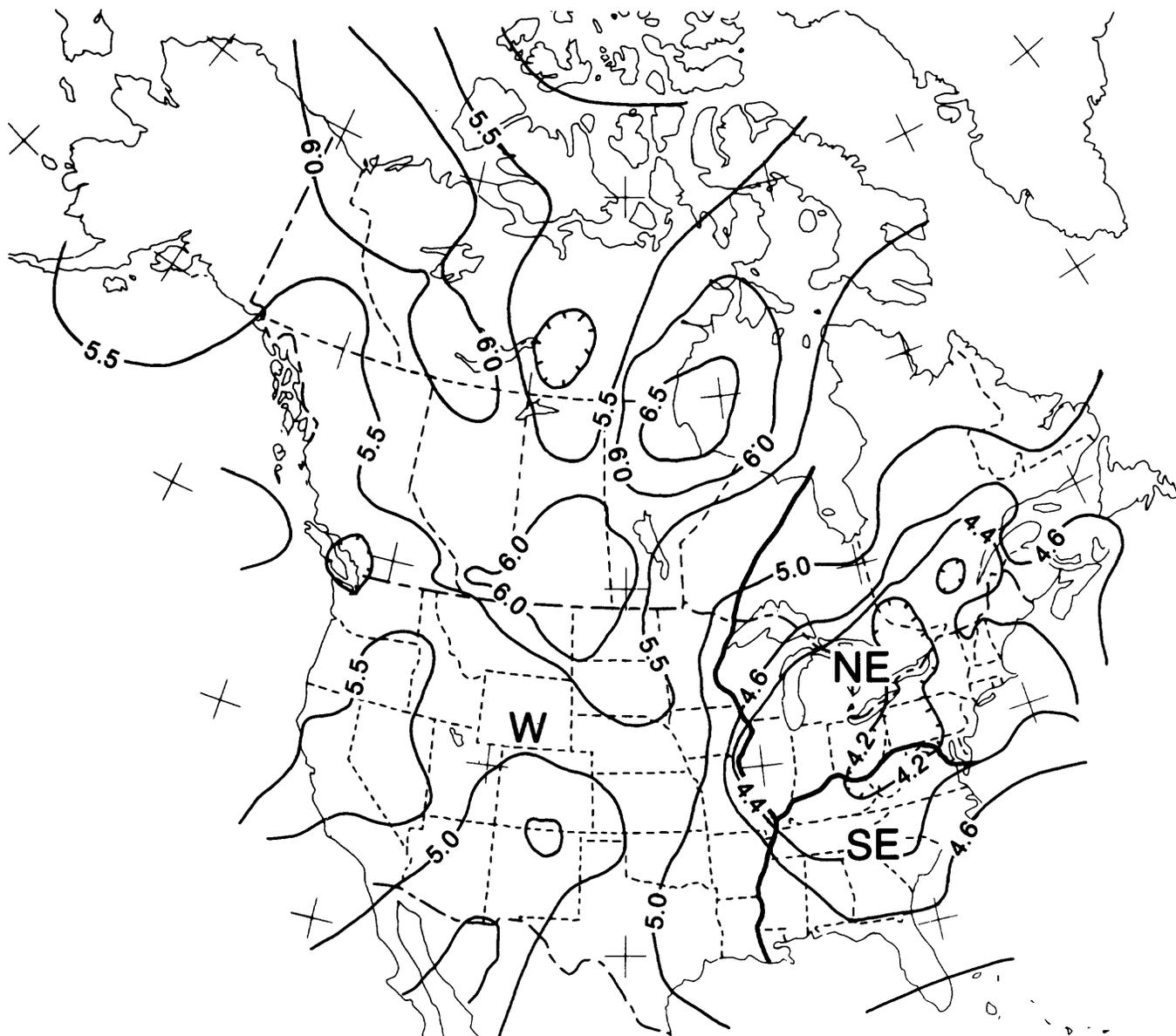
The data base for this geographic area (fig. 2) is the best documented, the most cited, and the most influential in addressing the acid-rain topic. Both mean-value and continuous-sampling data sets are available. Of the regional-scale data bases for which a reasonable degree of quality-control information is available, that collected in the period 1955–56 (Junge and Gustafson, 1956; Junge, 1958; and Junge and Werby, 1958) is the oldest. Later multisite synoptic data sets include those reported by Lodge and others (1968), Gambell and Fisher (1966), and Pearson and Fisher (1971). These data, combined with subsequent data from numerous sources, form the principal basis for the hypothesis that precipitation has undergone acidification both in intensity and areal extent during the past few decades (Cogbill, 1976; Cogbill and Likens, 1974; Likens, 1976; Likens and others, 1979; and Likens and Butler, 1981). Acidification has been inferred because of differences in pH relative to a presumed value of the natural pH of about 5.6, and because of differences in

pH among the synoptic data sets as a function of time and location (figs. 2 and 3). Although the assumption of a natural precipitation pH of 5.6 is unsupported, pH isopleths less than about 5.0 (Cogbill and Likens, 1974) probably delineate areas of anthropogenically acidified precipitation. In 1955–56, this included the area bounded by Ohio on the west, North Carolina on the south, and Maine on the northeast.

The importance of the regional synoptic data sets from 1955 to 1966 in the hypothesis of regional acidification of precipitation has resulted in several thorough reviews of potential errors and biases that may complicate the comparison of these early data with more recent data. Perhaps the most serious potential problem is the necessity of using calculated pH values for data lacking direct measurement. An error analysis by Liljestrand and Morgan (1979) indicated that, assuming a coefficient of variation of 10 percent in the major-ion data used to compute pH in early data sets, the 68.3-percent confidence limits at an actual pH of 5.65 are 5.17 and 6.13. The errors in calculation of pH are much smaller for more acidic pH values. Thus, errors should be greatest for southeastern and midwestern sites with pH values greater than 5.0, and least for the very acidic northeastern sites. Assuming the coefficient of variation is not larger than 10 percent, the authors conclude that the hypothesis of increasing acidity is valid for the northeastern United States from 1955 to 1966.

The errors associated with the analyses of individual elements in the synoptic data sets generally fall within a maximum range of 10 percent (Hansen and others, 1981). Analysis of additional sources of error (Hansen and others, 1981; Hansen and Hidy, 1982) indicate possible systematic error in pH of up to 0.2 and random error of 0.7 in the 1955–56 data for pH, while the 1965–66 data are calculated to have a systematic bias of -0.6 and a random error of 0.5. These studies conclude that the data sets are of "... insufficient quality and quantity to support any long-term trends in precipitation-acidity change in the eastern United States. However, the observations do show that precipitation is definitely acidic over this region, and is probably more acidic than expected from natural baseline conditions."

Although precipitation in parts of the Northeastern United States has been detectably acidified, the hypothesis that there has been a rapid expansion of this acidification to the south and west is less certain. The basis for the hypothesis is the difference in precipitation pH calculated from the data of Junge and Gustafson (1956) and the measured or calculated pH values from numerous later sources (Likens and Butler, 1981). The proposed acidification of



EXPLANATION

— 6.0 — Line of equal pH value,  
contour interval in 0.2  
and 0.5 pH unit

————— Arbitrary region boundary

NE - Northeastern and Mid-  
western United States and  
Southeastern Canada

W - Western United States

SE - Southeastern United States

**Figure 2.** Precipitation weighted, average annual pH of precipitation in North America, January-December 1981; and arbitrary boundary for regions addressed in this report. Isopleth map based on data from National Atmospheric Deposition Program and Canadian Network for Sampling Precipitation, reproduced by permission of the National Atmospheric Deposition Program.

precipitation in the Southeast since the mid-1950's will be discussed in a following section of this report.

Acidification since the mid-1950's in the Midwest has been critically evaluated in several reports. There are problems in defining pH isopleths for the Midwest because of low density of data points and because data are "almost exclusively ...from the urban Chicago and Cincinnati sites..." (Hansen and Hidy, 1982). The authors further analyze and attempt to quantify systematic and random errors associated with the measurement and calculation of pH, concluding (as noted previously) that the data are insufficient to support the westward expansion of acidification.

The influence of dust, enhanced by the drought of the mid-1950's was evaluated for a site in central Illinois (Stensland, 1980). Between 1954 and 1977, a minor increase in emission-related sulfate, a 50-percent increase in emission-related nitrate, and an 85-percent decrease in soil-derived calcium plus magnesium were observed. The

decrease in pH from 6.05 in the mid-1950's to recent (1978) values of about 4.1 was attributable almost entirely to the decrease in alkaline dust. The historical pH was calculated to be 4.2 instead of 6.05 after adjustment for the change in concentration of calcium plus magnesium caused by drought.

The influence of climatic variation on the data collected during the mid-1950's was further investigated for sites in Illinois, New York, Pennsylvania, and Virginia (Stensland and Semonin, 1982). In all cases, there was an increase of 30 to 72 percent in the concentration of nitrate and a larger (73 to 88 percent) decrease in the concentration of calcium plus magnesium between the mid-1950's and the late 1970's. Sulfate increased at the Illinois site, but decreased by 3 to 23 percent at the other sites. Thus, changes in the contribution of alkaline materials from natural sources is as probable a cause for observed changes in pH as is an increase in acidic materials

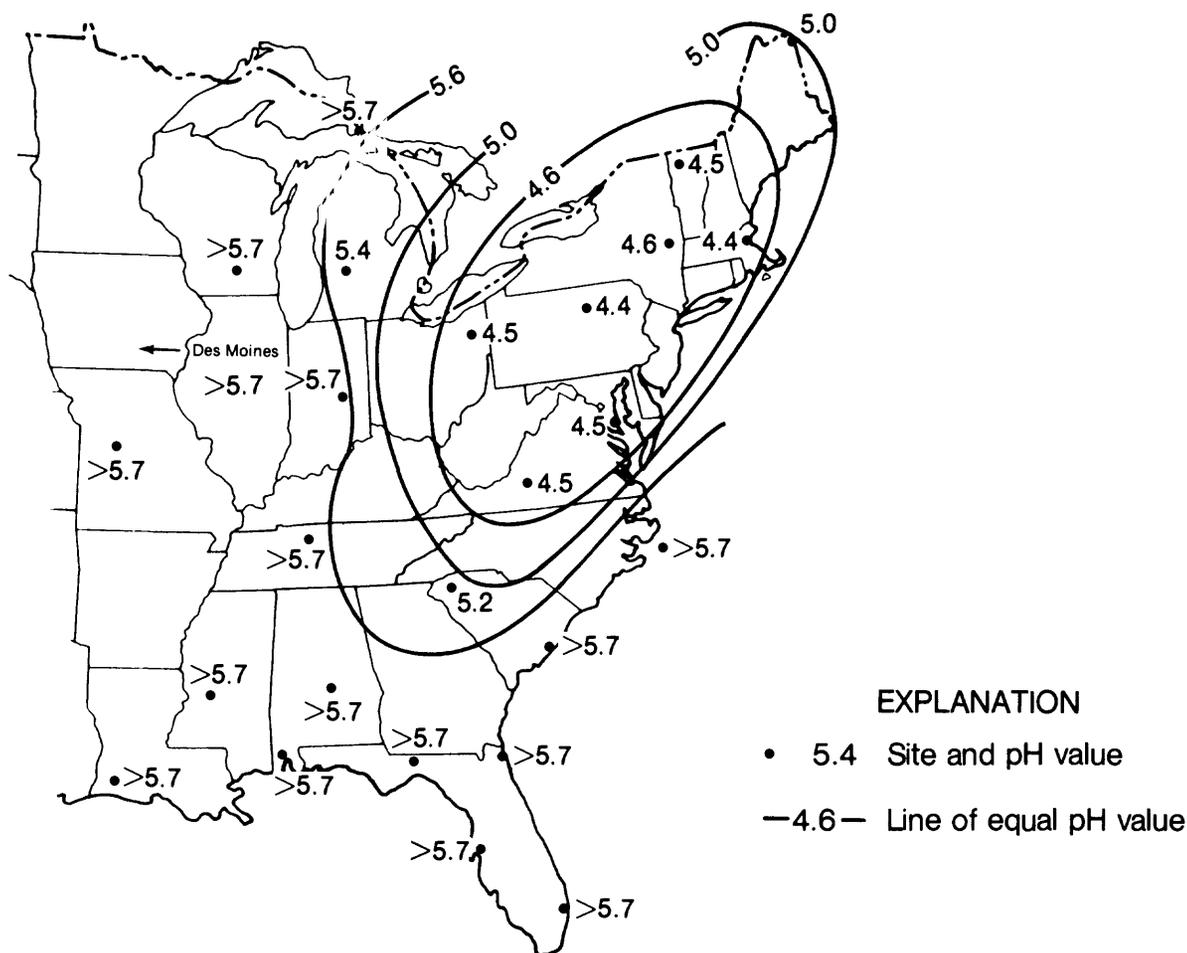


Figure 3. Isopleth map of pH based on H<sup>+</sup> concentrations calculated by Likens and Butler (1981) for the 1955-56 precipitation data.

from emissions sources. On a chemical equivalent basis, the change in alkaline materials is greater than the change in acidic materials.

Although most historical data on precipitation chemistry for this region of North America are from the United States, some data are available from Canada. Data for the period 1952–54 are available for Kentville, Nova Scotia (Herman and Gorham, 1957), indicating an average pH of about 5.7. Collection in copper rain gages, which were used in the Canadian study, rapidly neutralizes acidic solutions and produces pH values much greater than those of the initial solution (Kramer and Tessier, 1982). Thus, the measured pH data from this study do not necessarily indicate nonacidified precipitation during the early 1950's.

More recent data from Canada (Summers and Whelpdale, 1976; Dillon and others, 1978) indicate pH values much less than those expected for unacidified precipitation, averaging from about 4.0 to about 5.0. Unfortunately, the lack of reliable historical data severely limits the ability to estimate either the time of the onset of acidification or the acidification rates.

#### **Continuous-Collection Data Indicating Trends in Precipitation Acidification**

Although continuous-collection data sets have some of the problems of synoptic data sets, time-trend analysis on continuous sets often can avoid problems such as systematic error from methodology changes, the effects of short-term climatic variations and seasonality, and other problems that complicate the interpretation of changes in synoptic data sets. Examples of these problems were demonstrated by conflicting short-term trends in pH (Likens and others, 1980), step-function changes in nitrate concentration associated with analytical changes (Peters and others, 1982), and major effects on the statistical significance of trends caused by climatological extremes at the beginning and end of a record period (Likens and others, 1980).

Most of the time-trend analyses of continuous-collection data sets have concentrated on data from the Hubbard Brook Ecosystem Study (Likens and others, 1980), which commenced in 1963, and on the data from a multi-site network of stations operated by the U.S. Geological Survey in New York and Pennsylvania beginning in 1965 (Peters and others, 1982). After careful consideration is given to problems complicating the interpretation of data, both data sets continue to show significant trends in precipitation chemistry. Comparison of the two data sets indicates the value of comparing data from several sites, and of having an extensive period of record, before making generalizations on time trends in precipitation quality.

The Hubbard Brook data indicate no time-trend in pH during the 1964–77 period, although short-term trends

within this period "would have given conclusions conflicting with one another and with the lack of trend for the entire period" (Likens and others, 1980). The U.S. Geological Survey data (Peters and others, 1982) indicate a slight decrease in pH of about 0.2 at the stations in western New York, with a corresponding increase at the eastern New York sites, over the period 1965–78. Using linear time-trend analysis, both data sets indicate a decrease in sulfate concentrations, with three of the New York sites showing declines and only one showing an increase. Use of the nonparametric seasonal Kendall test on the New York data yielded a decrease in sulfate concentration at six sites and an increase in sulfate concentrations at one site (Peters and others, 1982). The Hubbard Brook data indicate "nitrate concentrations in precipitation increased rather markedly after 1964...but have not increased much since about 1970–1971" (Likens and others, 1980), while the New York data "suggest that nitrate increased at eight of nine stations" (Peters and others, 1982). An analytical methodology change in 1969 may have accounted for some of the supposed increase in nitrate in the U.S. Geological Survey data.

In assessing the role of various ions as possible controls on the acidity of precipitation, regression analyses of nitrate and sulfate against hydrogen ion, on an equivalent basis, were performed for both the Hubbard Brook Study data and the U.S. Geological Survey data. For the Hubbard Brook Study data, the loading of sulfate correlates poorly with acid loading, with much of the correlation apparently a result of climate extremes in two of the years of data collection. Nitrate loading, however, correlates on an approximately equivalent basis with acid loading. The U.S. Geological Survey data indicate a better correlation between acid loading and sulfate than between acid loading and nitrate; however, only the nitrate data after the 1969 analytical method change were used for the correlation, while the entire period of record was used for the sulfate correlation.

Nitrate concentrations during the last 100 years, converted to normalized loading rates for eastern North America, indicate a substantial increase between about 1950 and 1970. The loading was approximately equal to calculated nitrogen oxide emissions from combustion processes (Brimblecombe and Stedman, 1982).

#### **Trends in Surface-Water Acidification**

This topic has been very thoroughly discussed in two recent summary reports (United States-Canada Impact Assessment Working Group 1, 1983; U.S. Environmental Protection Agency, 1983b). The reader is referred to these two documents for additional detail on the summary presented here. Reference is also made to studies not included in the two summary reports.

As with precipitation chemistry, both synoptic and continuous-collection data bases are available. Comparisons, especially between synoptic data bases, are complicated by many of the same factors affecting synoptic precipitation-chemistry data sets—for example, climatic variations, changes in analytical methodology, and seasonality. An excellent review of problems caused by changes in analytical methodology and suggestions on how to quantitatively correct for many of the problems is presented by Kramer and Tessier (1982).

As shown in the summary reports (United States-Canada Impact Assessment Working Group 1, 1983; U.S. Environmental Protection Agency, 1983b), trends in surface-water chemistry of this region commonly indicate decreases in alkalinity and pH. Many of the Canadian studies cited in the two reports document aquatic-chemistry changes that may be caused by local sources of emissions—for example, the Sudbury smelting operations and emissions from municipalities near the lakes studied (Beamish and Harvey, 1972; Beamish and others, 1975; and Watt and others, 1979). Other studies found similar changes in chemistry for systems thought to receive precipitation loading derived from more regionally representative air masses—for example, Clear Lake and Walker Lake in south-central Ontario are shown to have decreased in alkalinity from about 1970 to 1976 (Dillon and others, 1978). If the data are examined for changes in acidic anions, however, only the data for Clear Lake indicate sufficiently large changes in the concentration of sulfate to account for the supposed change in alkalinity. Other lakes in the vicinity showed alkalinity values less than 200  $\mu\text{eq/L}$  (microequivalents per liter); however, data were not available to indicate historical values (Dillon and others, 1978). Time trends in the chemistry of 11 rivers in Atlantic Canada, primarily in Nova Scotia and Newfoundland, indicate no trends or decreasing trends in pH for the eight rivers having the least alkalinity. Sulfate trends were roughly balanced among decreasing, increasing, and stationary concentrations (Clair and Whitfield, 1983).

Data on trends in surface-water chemistry that may be related to precipitation chemistry indicate decreases in pH and alkalinity of lakes in New England and New York over the period from the 1930's to the 1970's (Davis and others, 1978; Norton and others, 1981; Burns and others, 1981; Schofield, 1976; and Pfeiffer and Festa, 1980). These have been recently reviewed and summarized (United States-Canada Impact Assessment Working Group 1, 1983; U.S. Environmental Protection Agency, 1983b). Although climatic and seasonal effects on pH and alkalinity generally are not addressed adequately in these reviews, the effects of changes in measurement techniques on reported pH are considered. Use of both modern and historical pH-measurement techniques (Norton and others, 1981; Burns and others, 1981; and Pfeiffer and Festa,

1980), as well as consideration of systematic errors in colorimetric pH measurements (Kramer and Tessier, 1982), indicate the reported decreases in pH since the 1930's probably are correct. Unfortunately, few historical alkalinity data are available in these studies; however, the data that exist indicate decreases of approximately 100  $\mu\text{eq/L}$ .

Acid precipitation is credited with the alkalization of Weber Lake in Michigan. Nitrate uptake by plants and sulfate reduction by bacteria are reported to have increased the rate of carbonate weathering at Weber Lake, where "...Weathering rates have increased as an indirect result of acid precipitation" (Kilham, 1982).

Data also are available for streams in the Northeastern United States. Data for nine streams having a wide variety of land use and geographically distributed across New York State were examined for trends in chemistry (Peters and others, 1982). After correcting for the effects of stream discharge on chemical concentration, statistically significant decreases in sulfate concentration were found for seven of the streams from the mid-1960's to the mid-1970's. Alkalinity values increased in three streams and decreased in one stream. Nitrate values showed no consistent trend. The mean alkalinity at the sites was relatively large, ranging from 170 to over 3,900  $\mu\text{eq/L}$ . Thus, the lack of any consistent trend in hydrogen-ion activity and, to a lesser extent, alkalinity, is not unexpected. Hydrogen-ion activity would be an insensitive measure of acidification in these moderately- to well-buffered streams. Natural variations in alkalinity seemingly are great enough to overshadow the slight fluctuations in precipitation acidity shown for this region (see preceding sections on trends in precipitation acidification for the Northeastern United States).

Data for pH are available from a U.S. Geological Survey Hydrologic Bench-Mark station and a second head-water stream in New Jersey (Johnson, 1979; Smith and Alexander, 1983). The pH values are low enough that the presence of bicarbonate buffering should be negligible. Thus, hydrogen-ion activity would respond in direct proportion to additions of acid and be a sensitive indicator of acidification. Johnson (1979) regressed pH against time for the two stations for the period 1963–1978. The results showed increases in hydrogen-ion concentrations at both stations, which ranged from 26 to 80  $\mu\text{eq/L}$  depending upon how the data were censored. Smith and Alexander (1983) subsequently analyzed the Hydrologic Bench-Mark data for the period 1973–1981 (excluding pH values prior to 1973 which were measured in the laboratory instead of the field) and found no trend in pH. The same authors also analyzed other data collected at the site beginning in 1966 and found an increase in alkalinity and a decrease in sulfate.

Two reports are available on the chemistry of streams in Pennsylvania (Arnold and others, 1980; Ritter and Brown, 1981). The former report has been extensively criticized (U.S. Environmental Protection Agency, 1983b); deficiencies reported were primarily a failure to discuss sites at which pH and alkalinity showed no trends or increasing trends, and the inclusion of very short-term changes (for example, 1 year) in the comparisons. Three hundred and fourteen stations were found which had data for at least two samples collected at least 1 year apart. Of this total, 207 stations showed a decrease in neither pH nor alkalinity, whereas the remaining 107 stations showed a decrease in either pH, alkalinity, or both. Although the data at two-thirds of the stations are consistent with no increase or a decrease in acid deposition, the deficiencies of the study render the results inconclusive.

The second report on trends in the chemistry of Pennsylvania streams (Ritter and Brown, 1981) compared samples collected during low-flow conditions in 1979–80 with samples collected prior to 1971. After selection of historical samples representing similar flow and specific conductance, most sample comparisons indicate a decrease in sulfate and alkalinity and possibly an increase in pH. Rigorous testing of the changes was not performed, although the graphical methods seem convincing for sulfate and alkalinity. However, the selection of the time period of low-flow, although simplifying the comparison of data, may have biased the data to the period of least sensitivity to acidification effects. The enhanced opportunity for soil-water interactions to prevail during these conditions would be expected to influence the pH and alkalinity. The results of this study are also inconclusive.

A wide array of stream chemistry data are available in the Northeast from eight stations of the national Hydrologic Bench-Mark Network (Smith and Alexander, 1983). Depending on the station, the alkalinity and pH records are continuous since the mid- to late 1960's, whereas records of field-measured pH are continuous since the late 1960's or early 1970's. Trend analysis testing showed a general regional pattern of increases in alkalinity, decreases in sulfate, and mixed results for pH. Collectively, the results suggest a decrease in acid deposition in the Northeast since the mid- to late 1960's.

## **Southeastern United States**

### **Trends in Precipitation Acidification**

Changes in the acidity of precipitation for this region are inferred from differences in synoptic data bases (figs. 2 and 3). The general geographic expansion of acidification cited in the previous section for the Midwestern United States has also been hypothesized for the Southeastern United States (Likens and Butler, 1981). The his-

torical synoptic data set is that of Junge and Gustafson (1956), while a composite of measured and calculated pH values obtained later was used to indicate change. Error analysis indicates that this approach is inconclusive for the Southeastern United States "...because of the uncertainty in the calculated values around pH 5.6," where both random and systematic errors in the calculation of precipitation pH are largest (Liljestrand and Morgan, 1979). Thus, comparison of historical and recent data must be supplemented with indirect data, such as the pH range of natural precipitation, to deduce trends in acidification.

Additional comparisons to the synoptic data of the mid-1950's have been made for Gainesville, Fla. (Hendry and Brezonik, 1980) and other sites throughout Florida (Brezonik and others, 1980). Average values of pH ranged from about 4.5 in northern Florida to about 5.5 in southern Florida. Sulfate concentration increases since the mid-1950's are hypothesized to account for most of the present acidification; however, increases in nitrate concentration are shown to be much larger as a percentage of the base period (Brezonik and others, 1980). In the analysis of data collected in Florida and other areas in the Southeastern United States, it was concluded that "On an areawide basis there is an apparent decrease of approximately 1 pH unit between the 1950's and 1970's" (Hansen and Hidy, 1982). The increase in acidity was attributed either to changes in climate, thereby affecting the proportion of low pH marine air to continental air, or to increases in population, motor vehicles, and power production.

In an analysis of spatial variation in precipitation chemistry in coastal South Carolina, the average pH was found to be about 4.3 (Richter and others, 1983). Sulfate deposition was approximately four times the nitrate contribution and, even with the coastal location, oceanic sulfate accounted for only about 9 percent of the total sulfate loading.

### **Trends in Surface-Water Acidification**

In a comparison of pH and alkalinity data collected in North Carolina during the early 1960's with data from the same sites during 1979, no significant change in pH was detected (Burns and others, 1981). The authors attributed the lack of change in pH to the fact that significant amounts of alkalinity (average alkalinity = 80  $\mu\text{eq/L}$ ) were available; thus, pH would be an insensitive indicator of acidification status.

To determine if the alkalinity concentrations were different between the two data sets, Burns and others (1981) first addressed the effects of changes in analytical methodology. In the early 1960's study, a methyl-orange colorimetric technique was used to determine the alkalinity endpoint; however, in the 1979 study an electrometric endpoint determination was used. The authors subtracted 32

$\mu\text{eq/L}$  of alkalinity from the historical data to correct these data for the amount of free hydrogen ion in solution at the presumed endpoint pH of 4.5. After making this correction, the authors noted a statistically significant ( $p = 0.02$ ) decrease in alkalinity concentration of about  $34 \mu\text{eq/L}$ . The correction used by the authors has since been shown to be in error (Kramer and Tessier, 1982). The appropriate correction in dilute samples is approximately  $81 \mu\text{eq/L}$ , rather than  $32 \mu\text{eq/L}$ , because the methyl-orange endpoint in dilute solutions is at a pH of about 4.0 rather than 4.5. If this larger correction value is subtracted from the historical data, the trend in alkalinity is an increase rather than a decrease in recent years (Kramer and Tessier, 1982). Thus, neither the pH nor alkalinity values indicate acidification between the early 1960's and 1979.

A comparison of alkalinity concentration to the sum of the four major cations, in  $\mu\text{eq/L}$ , also was made to estimate the degree of acidification (Burns and others, 1981). A ratio of about 1 would indicate that most chemical weathering was the result of reaction between carbon dioxide and soil minerals. Ratios much less than 1 would indicate weathering by other acids, such as those from acid rain. The observed ratio of 0.562 was interpreted to indicate that some acidification had taken place. Data pertaining to this ratio were unavailable from the historical data base. The ratios for two areas presumed to be acidified were 0.064 (Scandinavia) and 0.185 (La Cloche Mountains, Canada), while three presumably unacidified regions yielded ratios of 0.776 to 0.942. To be used as an index of acidification, no significant amount of anions other than bicarbonate can be derived from chemical weathering or from precipitation, unless balanced by an equivalent amount of hydrogen ion in precipitation. Burns and others (1981) provide no information to indicate whether these conditions were met.

In an analysis of trends in the chemistry of the Neuse River, N. C., an increase of approximately 50 percent in sulfate concentration from 1955 to 1975 was noted (Harned, 1982); this increase was attributed to atmospheric loading. No comparison of the sulfate concentration in precipitation was made to indicate the appropriateness of the magnitude; however, other work in the same area (Munger and Eisenreich, 1983) indicates sulfate concentrations in precipitation of about 1.5 to 2.0 mg/L (milligram per liter). Considering that the probable level of evapotranspirative enhancement in the area is around 2–3, a significant part of the sulfate concentration of 10 mg/L in the Neuse River most likely results from precipitation loading.

Thirteen lakes in northern Florida were shown to be significantly different in pH from seven lakes in southern Florida (Crisman and others, 1980). The authors attribute the difference to variations in acidity of precipitation

in the two areas; however, no data are presented to indicate that the lake groups should be comparable. The authors also state that pH and alkalinity in the northern Florida lakes have decreased during the last 20 years, while sulfate concentrations have increased. No documentation for the conclusions was provided in the report.

On a regional basis, stream chemistry data are available in the Southeast for nine stations of the Hydrologic Bench-Mark Network (Smith and Alexander, 1983). Collection of data began between the mid-1960's to the early 1970's, depending upon the station and the specific chemical constituent. Trend analysis testing for the nine stations has yielded a regional picture for pH which is balanced between decreases and no change; a mixed picture for alkalinity, with an equal number of increases, decreases, and no change; and a definite regional trend of increases in sulfate. Collectively, the Bench-Mark data in the Southeast are consistent with an increase in acid deposition over the period of record.

## Western North America

### Trends in Precipitation Acidification

Precipitation chemistry for this region is documented at a few sites, but only for the very recent time period. Although the region logically could be divided into numerous smaller areas based on differences in emission sources, the lack of data limits the usefulness of this approach. The first documentation of trends in the region is for the area 6 kilometers east of the Continental Divide in Boulder County, Colo. (Lewis and Grant, 1980). During a period of 150 weeks beginning in 1975, weekly bulk deposition samples indicated a linear decrease of about 0.8 in pH. The magnitude of the hydrogen-ion loading increase was balanced by an equivalent increase in the loading of nitrate. Sulfate did not have a significant ( $P = 0.05$ ) trend with time, and was only slightly greater in loading rate than was nitrate—196 compared to 129 equivalents per hectare per year (Grant and Lewis, 1982).

The lack of additional stations in the area complicated the assignment of source areas. There was further complication because of the proximity to the highly urbanized Denver Front Range metropolitan area (Lewis and Grant, 1980; Kelly and Stedman, 1980). Although a detailed meteorological study of the relationship of episodic upslope wind to precipitation chemistry was not available for the period of study reported by Lewis and Grant (1980), a study of the relationship was made by Kelly and Stedman (1980). The results showed that from January to July, when upslope conditions are the most prevalent, a hundredfold increase in concentrations of pollutants in air masses from the metropolitan area is the main factor influencing average concentration during collection

periods of about a week, such as was employed in the work of Lewis and Grant (1980). In reply to Kelly and Stedman (1980), Lewis and Grant (1980) agreed that the effect of metropolitan contributions are a "...potential source of the mineral acids in precipitation near the Continental Divide, but very forceful and frequent year-round upslope movements are required, against strong prevailing weather patterns in certain months, in order to account fully for the acidity...." The possible problems associated with the extrapolation of short-term trends in precipitation chemistry were illustrated by the Hubbard Brook data (Likens and others, 1980). Thus, the results of these observations should be considered indicative only of the 1975-78 period. To determine the relative importance of regional air masses to local ones, additional sites, a longer period of record, and combined meteorological/precipitation-chemistry studies will be required.

Very recently, a detailed meteorological study of atmospheric and precipitation chemistry was performed in the areas studied by Lewis and Grant (Huebert and others, 1983). These authors concluded, "Thus, although the wind is from the east only a small fraction of the time, the almost order-of-magnitude greater  $\text{NO}_x$  and  $\text{HNO}_3$  concentrations associated with these winds imply that at least 60 percent of the total concentration of these species during the entire observing period came from sources to the east. This is a conservative percentage since it does not include concentrations observed during light and variable wind conditions, which do include some short duration and weak east-wind conditions."

Short-term data are available for the area near Gothic, Colo. (John Harte, Lawrence Berkeley Laboratory, written commun., 1983). The average pH in samples collected since 1980 and weighted for the amount of precipitation, is 4.55. The nitrate-to-sulfate equivalent ratio, which averages 0.9, is greater than the 0.7 value reported east of the Continental Divide (Grant and Lewis, 1982). Although the time period for trend determination was insufficient, the average pH is lower than expected at remote sites (Galloway and others, 1982; Charlson and Rodhe, 1982).

The volume-weighted mean pH of precipitation samples collected in Pasadena, Calif., from 1976 to 1977 was 4.06 (Liljestrand and Morgan, 1978). The average nitrate-to-sulfate equivalent ratio was 1.25, or 1.32 after subtraction of the marine sulfate component. The authors noted the period of collection was one of anomalous weather. A drought occurred during the sampling period, and two individual storms accounted for 20 percent of the total precipitation. Because the site is urban, the results are unlikely to be representative of the region.

During January through July 1981, the average pH at five sites in the Cascade Mountains east of Puget Sound, Wash., was about 4.7, with an average nitrate-to-

sulfate equivalent ratio of 0.8. The ratio was about 0.7 after subtraction of the marine sulfate component (Logan and others, 1982). Although the period of data collection was brief, the data indicate slightly more acidic conditions than the lower limit estimated for unpolluted remote sites.

Precipitation in the east-central Sierra Nevada Mountains was acidic (pH of 3.7 to 4.9) during convective storms in the summer of 1981 (Melack and others, 1983). During this period, sulfate accounted for about twice as much acidity as did nitrate. Urban and agricultural sources within California are the supposed sources of the acidity. Over 90 percent of the precipitation was shown to occur as snow with a pH near 5.7, reflecting the chemistry of large frontal storms from the Pacific Ocean. This occurs even though the pH of these frontal storms is significantly lower (pH less than about 5) as they pass over cities and agricultural lands west of the study area which are potential sources of acidic anions. Thus, much of the acidity from urban and agricultural sources is removed before air masses cross the Sierra Nevada Mountains.

### Trends in Surface-Water Acidification

Recent interest in possible acidification of surface water in the western half of North America has resulted in several studies of aquatic impacts and sensitivity. Broad-scale sensitivity maps indicate extensive areas in this region that should exhibit trends in aquatic chemistry in response to any sustained changes in precipitation chemistry (National Atmospheric Deposition Program, 1982; U.S. Environmental Protection Agency, 1983a).

At the Colorado site discussed by Lewis and Grant (1980), the rate of increase in hydrogen-ion loading to the Como Creek watershed was matched by an approximately equivalent decrease in stream transport of bicarbonate. The stream loadings of sulfate, nitrate, ammonia, and dissolved organic matter also showed significant increases during the study period. Total cation loading in the stream decreased enough to account for only about one-third of the observed decrease in alkalinity, indicating that much of the observed decrease in alkalinity was attributable to neutralization by hydrogen ion (Lewis and Grant, 1979).

In a 1979 reconnaissance of Colorado lakes sampled initially during the periods 1938-42 and 1949-52, there was a 17-percent decrease in alkalinity and a 0.2 unit decrease in pH. Both decreases were attributed to acidification of precipitation (Lewis, 1982). The author also attributes a 16-percent decline in "total residue" to acidification, with the mechanism being the removal of bicarbonate by strong acids. Although Lewis (1982) attempted to correct for seasonality and climatic variation, the method used may not have been appropriate. For example, if the correc-

tion for the 29-percent greater-than-average annual discharge were inadequate, bicarbonate and total residue would be expected to show approximately equal decreases due to simple dilution. More detailed chemical analysis would be necessary to determine whether bicarbonate has decreased disproportionately to other major constituents. The log-log plot of recent and former alkalinity (Lewis, 1982) indicates a seemingly constant percentage decrease in alkalinity between the two data sets, while acidification should cause a relatively greater percentage decrease in the alkalinity of the least-buffered samples. Methodology changes were estimated to produce an error or less than about 12  $\mu\text{eq/L}$ , although the methyl-orange method is calculated to have a systematically greater alkalinity than the electrometric method of about 50 to 80  $\mu\text{eq/L}$  (Kramer and Tessier, 1982). The average decrease in alkalinity of about 97  $\mu\text{eq/L}$  compares to the 17  $\mu\text{eq/L}$  free-acidity in precipitation at the Como Creek site (Lewis and Grant, 1979) if evapotranspiration of about 80 percent is assumed. Thus, although the data are compatible with the hypothesis that acidification of precipitation has caused the observed changes, other variables such as climate could also explain the changes.

At two reservoirs east of San Francisco, Calif., decreases in pH and alkalinity have occurred since about 1945 (McColl, 1981). The alkalinity decrease at Pardee Reservoir amounted to about 120  $\mu\text{eq/L}$  between 1944–79. The author attributes the decrease to  $\text{NO}_x$  emissions from the highly developed San Francisco area, although lack of data on nitrate and sulfate concentrations in the reservoirs prevented direct evaluation of the issues.

In a 1981 reconnaissance of lakes in the Cascade Mountains of central Washington, acidification status was estimated by comparing calcium to bicarbonate (Henriksen, 1979). Lake alkalinities were found to be low (4 to 190  $\mu\text{eq/L}$ ), although no evidence of acidification was found (Logan and others, 1982).

A reconnaissance of lakes in the east-central Sierra Nevada Mountains during the summer of 1981 showed the lakes to be sensitive to acidification; however, a lack of historical data prevented evaluation of any trends in their chemistry (Melack and others, 1983).

On a regional basis, stream chemistry data are available in the West for 30 stations of the Hydrologic Benchmark Network. Trend analysis testing of the data showed a mixed regional picture for pH, but a general regional pattern of decreasing alkalinity and increasing sulfate (Smith and Alexander, 1983). As would be expected, the downward trends in alkalinity were most prevalent among stations with relatively low mean alkalinity. The Benchmark Network results are consistent with an increase in acid deposition in the West over a period of about the last 15 years.

## DISCUSSION

From the information presented in the Results section of this report, it is apparent that differences exist in both the status of acidification and in the presence or absence of recent temporal trends among the geographic regions considered. Most of the controversy in the literature reflects alternative hypotheses to explain an inadequate historical data base, rather than criticism of inadequate or biased work. As a result, the following questions can be addressed by the cited literature:

1. Are temporal trends in acidification of precipitation evidenced? If so, is this a continental-scale, regional, or local phenomenon?
2. Are temporal trends in acidification of surface water evidenced? If so, is the same geographic distribution in item 1 applicable to changes in surface-water chemistry?
3. Are there apparent conflicts in trends of acidification of precipitation relative to acidification of surface water?

As presented in the regional sections on trends in precipitation acidification, the hypothesis of an increase in precipitation acidity in the Northeastern United States has been advanced, tested, and found to be substantiated by several studies, for which there are two main claims:

1. The precipitation is more acidic than it would be in the absence of anthropogenic emissions.
2. The area of greatest acidification of precipitation has rapidly expanded to the Southeast and Midwest during the last few decades.

Of these two claims, the first is readily validated by the information presented previously in this report. The evidence consists primarily of:

1. The measured acidity of precipitation relative to that (a) found in precipitation in remote parts of the world, and (b) predicted on the basis of natural geochemical cycles of strong acids; and
2. The comparison of precipitation chemistry from stations operated in the 1960's and 1970's to synoptic data from the mid-1950's.

The second claim is less readily addressed by the available data. Evaluation of the hypothesis of recent expansion of acidification to the Southeast is complicated by meager data. Present data from both individual researchers and national monitoring networks indicate acidity levels, from the Carolinas to Florida and westward into Alabama and Georgia, that are more acidic than would be expected for sites unaffected by anthropogenic emissions. In addition, comparison of these data with the meager historical data suggests, but does not unambiguously prove, increased acidification since the 1950's.

Evaluation of the hypothesis of recent expansion of acidification to the Midwest is severely complicated by the effects of climatic fluctuation on the only historical

data. It is unclear whether the data are capable of providing an unambiguous test of the hypothesis.

Although definitive data do not exist to address the timing of acidification of precipitation in the Midwest and Southeast, data are available to examine trends in the Northeast since about the mid-1960's. These data indicate no significant change in precipitation acidity in the most acidified section of this region. Decreases in sulfate and increases in nitrate concentrations are well documented during the same time period. With respect to the initial acidification of the Northeast, the available data indicate this occurred before the mid-1950's; however, no unambiguous documentation has been presented to refine the estimate of acidification status prior to this period. It is difficult to estimate the reliability of data previous to the mid-1950's because of problems with inappropriate methodology and inadequate analysis schemes. The few data prior to the mid-1950's tend to address agricultural needs and provide little documentation on reliability.

In the Western United States, the level of precipitation acidity or the results of very short-term trend estimates indicate that individual sites have probably been acidified by anthropogenic emissions. Acidification noted by several studies (Lewis and Grant, 1980; Liljestrand and Morgan, 1979; Logan and others, 1982) generally has been attributable to localized sources, even though the sites seem remote. The time of initial acidification is not defined by these studies.

The hypothesis of an increase in the acidity of surface water has been advanced and, to some extent, tested. However, the degree of examination of alternative hypotheses has not advanced to the level achieved for precipitation chemistry.

In Canada, the best documented cases of acidification are lakes for which the acidification is attributable to local emissions. However, published information on a few lakes indicates that acidification since the mid-1960's may be attributed to regional sources (Dillon and others, 1978). Several rivers in Atlantic Canada exhibit recent declines in pH, although no consistent trends in sulfate concentrations exist for these rivers (Clair and Whitfield, 1983). While published trend information on precipitation acidity in this section of Canada is seemingly unavailable, trend information at nearby sites in the United States indicates no trend in acidity during this period (Likens and others, 1980; Peters and others, 1982).

Decreases in pH and alkalinity of lakes in New England and New York are well documented to have occurred sometime between the 1930's and the 1970's (Davis and others, 1978; Norton and others, 1981; Burns and others, 1981; Schofield, 1976; Pfeiffer and Festa, 1980). Hydrologic Bench-Mark data, collected beginning in the mid-to late 1960's, show a general pattern in the Northeast of increases in alkalinity and decreases in sulfate. In streams of New York State, acidification trends appear

to be negligible for the period from the mid-1960's to the mid-1970's, and sulfate concentrations decreased (Peters and others, 1982).

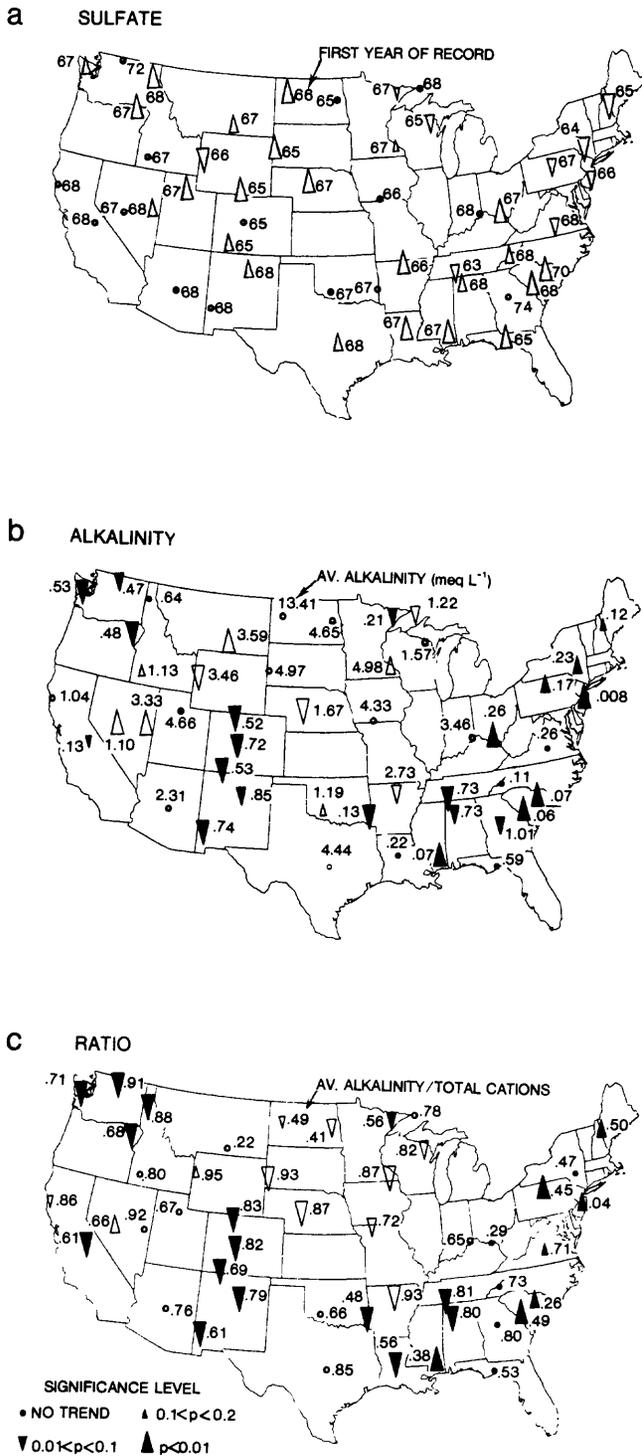
In New Jersey, trend tests on data from a Hydrologic Bench-Mark station showed an increase in stream acidity for the period of 1963 through 1978 (Johnson, 1979), but the absence of a trend in pH for the period of 1973 through 1981 (Smith and Alexander, 1983).

The available information well documents a trend in surface-water acidification attributable to precipitation acidification in the Northeastern United States and Southeastern Canada. The Canadian sites mostly experienced acidification due to local sources. In the Northeastern United States, regional changes in precipitation chemistry apparently acidified lakes and streams in New England, New York, and New Jersey. The acidification appears to have occurred before the mid- to late 1960's, because data collected continuously since that time shows a lack of further acidification in New York streams (Peters and others, 1982), and a slight recovery of some acidified streams in scattered locations throughout the Northeast. The findings of these stream chemistry studies are consistent with a region-wide decrease in SO<sub>2</sub> emissions in the Northeast for the period 1965-1980 (Smith and Alexander, 1983).

In the Southeastern United States, most data on acidification of surface waters are ambiguous. An increase in sulfate has been documented in the Neuse River of North Carolina (Harned, 1982). Unfortunately, changes in pH and alkalinity of surface waters in North Carolina (Burns and others, 1981) give ambiguous results because of uncertainty in the effect of methodology on the value of historical data (Kramer and Tessier, 1982). Undocumented claims of acidification of Florida lakes have been published (Crisman and others, 1980).

In the West, most reports on the acidification of surface waters have reflected local conditions. A stream east of the Continental Divide, near Boulder, Colorado, has shown a decrease in alkalinity loading equivalent to the increase in hydrogen-ion loading from precipitation (Lewis and Grant, 1979). The source of acidity in the precipitation is estimated to be the local urban sources (Huebert and others, 1983). Ambiguous data indicate a decrease in alkalinity of lakes in the same general region of Colorado (Lewis, 1982). Two California reservoirs which receive precipitation influenced by local urban sources have been acidified (McColl, 1981).

In contrast to the earlier reports, the recently published work based on the Hydrologic Bench-Mark Network indicates regional trends in the chemistry of streams in the Southeast and the West. This report (Smith and Alexander, 1983) indicates that sulfate concentrations have increased in streams in both the Southeast and the West during the period since about the mid-1960's (fig. 4a). In both regions, there have been concurrent decreases in



**Figure 4.** Trends in (a) sulfate concentration, (b) alkalinity, and (c) the ratio of alkalinity to the sum of Ca, Mg, Na, and K concentration at Bench-Mark stations for the period of record through 1981. Symbols indicate direction and significance level of trends. Dark symbols in maps (b) and (c) indicate stations with mean alkalinity less than 1 meq L<sup>-1</sup> (modified from Smith and Alexander, 1983).

alkalinity (fig. 4b) and in the ratio of alkalinity to the sum of the major cations (fig. 4c). These chemical changes are consistent with the initiation of acidification in bicarbonate systems. In the Southeast, the meager data on precipitation chemistry suggest a regional pattern of recent acidification. However, the Bench-Mark Network results are the first indication of the possible regional acidification of surface waters. In the West, precipitation-chemistry data are unavailable for most of the region for the time period in question. Thus, although the Bench-Mark data suggest that regional acidification of surface waters may be occurring in the West, precipitation data are needed to test the hypothesis.

## CONSIDERATIONS FOR FUTURE ACID-PRECIPIATION NETWORKS

It is apparent from the discussion presented in this report that data limitations have been a major constraint in developing an understanding of the acidification of precipitation and surface water. The lack of trend information for surface-water systems in much of the country does not reflect a complete absence of data, but rather a lack of data on appropriate systems and chemical analysis by inconsistent methodologies. The period since the mid-1960's has been one of great increase in collection of both synoptic and repetitive data on the chemistry of surface water. Documentation of changes attributable to precipitation during this period, however, is limited to a relatively few studies by individual researchers and data from a 47-station nationwide network designed to detect changes in systems remote from local anthropogenic influences. Further data limitations result from a failure to examine the hydrologic system in its entirety; that is, concurrent precipitation and surface-water data generally are not available. Moreover, ground-water systems and process-oriented research have been ignored in most studies examined by this report.

The concept of the integral nature of hydrologic systems and the futility of examination of segments as self-sufficient systems is not new, but unfortunately, is neglected. This neglect has been largely influenced by the design of data-collection networks and individual studies to address the specific requirements of legislation. The period of great increase in chemical monitoring since the 1960's has seen these specific legislative requirements change from conventional sanitary indexes, to toxic metals, to toxic organic compounds in pace with control efforts and progress in analytical chemistry. Without doubt, there is need to address limited questions regarding compliance with legislation designed to protect both aquatic life and the general welfare. Unfortunately, the concentration of effort to address only these specific requirements has seriously hampered our understanding of what con-

stituent concentrations might be expected to occur naturally, and what temporal and spatial distributions we should see in the absence of anthropogenic sources. Only well-planned commitments to define natural controlling mechanisms in hydrologic systems will allow future problems to be addressed with an adequate historic data base. Recent reports on the effects of man on acidification at remote sites indicate that this commitment is needed soon and that site selection is much more difficult than previously has been supposed.

## SUMMARY

The acidity of precipitation in the Northeastern United States and Southeastern Canada has increased in the past, probably as a result of anthropogenic emissions. The increase in New England and New York occurred primarily before the mid-1950's. Since the mid-1960's there has been no significant change in the acidity of precipitation in this region; however, sulfate concentrations have decreased and nitrate concentrations may have increased. The time of initial acidification in Southeastern Canada is not known because of a lack of historical data. In the Southeastern United States, the evaluation of whether precipitation has been acidified is complicated by meager data. The available data show that precipitation is more acidic than would be expected for sites unaffected by anthropogenic emissions. In addition, comparison of recent data with the meager historical data suggests, but does not unambiguously prove, increased acidification since the 1950's. In the Western United States, available data indicate that precipitation at individual sites has been acidified by anthropogenic emissions. The acidification generally has been attributable to localized sources and the time of initial acidification is undefined.

Acidification of lakes and streams in the Northeastern United States has occurred in a time frame compatible with the hypothesis that acidification of precipitation was the cause. The acidification of surface waters appears to have occurred before the mid- to late 1960's. In Southeastern Canada, the best-documented cases of acidified lakes point to localized sources of acidic emissions as the cause. Sparse evidence of recent regional acidification of lakes and streams exists, but evidence for acidification of precipitation as the cause is largely lacking. In the Southeastern United States, most data on acidification of surface waters are ambiguous, and in the West, most of the data reflect local conditions. However, recent analysis of a national network of remote stream sampling stations indicates that, since the mid- to late 1960's, sulfate concentrations have increased in the Southeast and the West, with a concurrent decrease in alkalinity. Additional work is needed to test the hypothesis that regional acidification of surface waters is occurring in the Southeastern and Western United States.

## SELECTED REFERENCES

- Arnold, D. E., Light, R. W., and Dymond, V. J., 1980, Probable effects of acid precipitation on Pennsylvanian waters: Corvallis, Oreg., U.S. Environmental Protection Agency, EPA-600/3-80-012, 20 p.
- Beamish, R. J., and Harvey, H. H., 1972, Acidification of the La Cloche Mountain lakes, Ontario, and resulting fish mortalities: *Journal Fisheries Research Board of Canada*, v. 29, p. 1131-1143.
- Beamish, R. J., Lockhart, W. L., Van Loon, J. C., and Harvey, H. H., 1975, Long-term acidification of a lake and resulting effects on fishes: *Ambio*, v. 4, p. 98-102.
- Brezonik, P. L., Edgerton, E. S., and Hendry, C. D., 1980, Acid deposition and sulfate deposition in Florida: *Science*, v. 208, p. 1027-1029.
- Brimblecombe, P., and Stedman, D. H., 1982, Historical evidence for a dramatic increase in the nitrate component of acid rain: *Nature*, v. 298, p. 460-462.
- Burns, D. A., Galloway, J. N., and Hendry, G. R., 1981, Acidification of surface waters in two areas of the eastern United States: *Water, Air, and Soil Pollution*, v. 16, p. 275-285.
- Charlson, R. J., and Rodhe, H., 1982, Factors controlling the acidity of natural rainwater: *Nature*, v. 295, p. 683-685.
- Clair, T. A., and Whitfield, P. H., 1983, Trends in pH, calcium, and sulfate of rivers in Atlantic Canada: *Limnology and Oceanography*, v. 28, p. 160-165.
- Cogbill, C. V., 1976, The history and character of acid precipitation in eastern North America: *Water, Air, and Soil Pollution*, v. 6, p. 407-413.
- Cogbill, C. V., and Likens, G. E., 1974, Acid precipitation in the north-eastern United States: *Water Resources Research*, v. 10, p. 1133-1137.
- Cowling, E. B., 1982, Acid precipitation in historical perspective: *Environmental Science and Technology*, v. 16, no. 2, p. 110A-123A.
- Crisman, T. L., Schulze, R. L., Brezonik, P. L., and Bloom, S. A., 1980, Acid precipitation: the biotic response in Florida lakes, in Drablow, D., and Tollan, A., eds., 1980, *Ecological impact of acid precipitation: International Conference, Sandefjord, Norway, 1980, Proceedings: Oslo, Norway, SNSF project*, p. 296-297.
- Dailey, N. S., and Winslow, S. G., 1980, Health and environmental effects of acid rain—an abstracted literature collection, 1966-1979: Bethesda, Md., Federation of American Societies for Experimental Biology, 202 p.
- Davis, R. B., Smith, M. O., Bailey, J. H., and Norton, S. A., 1978, Acidification of Maine (USA) lakes by acidic precipitation: *Verh. Internat. Verein. Limnol.*, v. 10, p. 532-537.
- Dillon, P. J., Jeffries, D. S., Snyder, W., Reid, R., Yan, N. D., Evans, D., Moss, J., and Scheider, W. A., 1978, Acidic precipitation in southcentral Ontario: Recent Observations, *Journal Fisheries Research Board of Canada*, v. 35, p. 809-815.
- Environment Information Center, 1982, *Enviroline user's manual, appendix F, keyword lists*: New York, Environment Information Center, F1-F92.

- Galloway, J. N., and Cowling, E. B., 1978, The effects of precipitation on aquatic and terrestrial ecosystems—A proposed precipitation chemistry network: *Air Pollution Control Association Journal*, v. 28, no. 3, p. 229–235.
- Galloway, J. N., and Likens, G. E., 1981, Acid precipitation—the importance of nitric acid: *Atmospheric Environment*, v. 15, no. 6, p. 1081–1085.
- Galloway, J. N., Likens, G. E., Keene, W. C., and Miller, J. M., 1982, The composition of precipitation in remote areas of the world: *Journal of Geophysical Research*, v. 87, p. 8771–8786.
- Gambell, A. W., and Fisher, D. W., 1966, Chemical composition of rainfall, eastern North Carolina and southeastern Virginia: U.S. Geological Survey Water-Supply Paper 1535-K, 41 p.
- Grant, M. C., and Lewis, W. M., Jr., 1982, Chemical loading rates from precipitation in the Colorado Rockies; *Tellus*, v. 34, p. 74–88.
- Hansen, D. A., and Hidy, G. M., 1982, Review of questions regarding rain acidity data: *Atmospheric Environment*, v. 16, no. 9, p. 2107–2126.
- Hansen, D. A., Hidy, G. M., and Stensland, G. J., 1981, Examination of the basis for trend interpretation of historical rain chemistry in the eastern United States: Westlake Village, Calif., Environmental Research and Technology, Inc., ERT Document no. P-A097, 1 v.
- Harned, D. A., 1982, Water quality of the Neuse River, North Carolina—Variability, pollution loads, and long-term trends, in water quality of North Carolina streams: U.S. Geological Survey Water-Supply Paper 2185, p. D1–D44.
- Haurwitz, B., and Austin, J. M., 1944, *Climatology*: McGraw Hill, New York.
- Hendry, C. D., and Brezonik, P. L., 1980, Chemistry of precipitation at Gainesville, Florida: *Environmental Science and Technology*, v. 14, p. 843–849.
- Henriksen, Arne, 1979, A simple approach for identifying and measuring acidification of freshwater: *Nature*, v. 278, p. 542–545.
- Herman, F. A., and Gorham, E., 1957, Total mineral material, acidity, sulfur, and nitrogen in rain and snow at Kentville, Nova Scotia: *Tellus*, v. 9, p. 180–183.
- Huebert, B. J., Norton, R. B., Bollinger, M. J., Parrish, D. D., Hahn, C., Bush, Y. A., Murphy, P. C., Fehsenfeld, F. C., and Albritton, D. L., 1983, Gas phase and precipitation acidities in the Colorado mountains, in Hermann, R., and Johnson, A. I., eds., 1983, *Acid rain—a water resources issue for the 80's*: American Water Resources Association International Symposium, Denver, Colo., 1982, Proceedings, p. 17–23.
- Johnson, A. H., 1979, Evidence of acidification of headwater streams in the New Jersey Pinelands: *Science*, v. 206, p. 834–836.
- Junge, C. E., 1958, The distribution of ammonia and nitrate in rain water over the United States: *Transactions of American Geophysical Union*, no. 39, p. 241–248.
- Junge, C. E. and Gustafson, P. E., 1956, Precipitation sampling for chemical analysis: *American Meteorological Society, Bulletin* 37, 244 p.
- Junge, C. E., and Werby, R. T., 1958, The concentration of chloride, sodium, potassium, calcium, and sulfate in rain water over the United States: *Journal of Meteorology*, no. 15, p. 417–425.
- Kelly, T. J., and Stedman, D. H., 1980, Effect of urban sources on acid precipitation in the western United States: *Science*, v. 210, p. 1043.
- Kilham, Peter, 1982, Acid precipitation: Its role in the alkalization of a lake in Michigan: *Limnology and Oceanography*, v. 27, p. 856–867.
- Kramer, James, and Tessier, Andre, 1982, Acidification of aquatic systems—A critique of chemical approaches: *Environmental Science and Technology*, v. 16, no. 11, p. 606A–615A.
- Lewis, W. M., Jr., 1982, Changes in pH and buffering capacity of lakes in the Colorado Rockies: *Limnology and Oceanography*, v. 27, no. 1, p. 167–172.
- Lewis, W. M., Jr., and Grant, M. C., 1979, Changes in the output of ions from a watershed as a result of the acidification of precipitation: *Ecology*, v. 60, p. 1093–1097.
- 1980, Acid precipitation in the western United States: *Science*, v. 207, p. 176–177.
- Likens, G. E., 1976, Acid precipitation: *Chemical and Engineering News*, v. 54, no. 48, p. 29–44.
- Likens, G. E., Bormann, F. H., and Eaton, J. S., 1980, Variations in precipitation and streamwater chemistry at the Hubbard Brook Experimental Forest during 1964 to 1977, in Hutchinson, T. C., and Havas, M., eds., *Effects of acid precipitation on terrestrial ecosystems: NATO Conference on Effects of Acid Precipitation on Vegetation and Soils*, Toronto, Canada, 1978: New York, Plenum Press, p. 443–464.
- Likens, G. E., and Butler, T. J., 1981, Recent acidification of precipitation in North America: *Atmospheric Environment*, v. 15, no. 7, p. 1103–1109.
- Likens, G. E., Wright, R. G., Galloway, J. N., and Butler, T. J., 1979, Acid rain: *Scientific American*, no. 24, p. 43–51.
- Liljestrand, H. M., and Morgan, J. J., 1978, Chemical composition of acid precipitation in Pasadena, Calif.: *Environmental Science and Technology*, v. 12, no. 12, p. 1271–1273.
- 1979, Error analysis applied to indirect methods for precipitation acidity: *Tellus*, v. 31, no. 5, p. 421–431.
- Lodge, J. P., Jr., Pate, J. B., Basbergill, W., Swanson, G. S., Hill, K. C., Lorange, E., and Lazrus, A. L., (1968), *Chemistry of United States precipitation—Final report on the National Precipitation Sampling Network*: Boulder, Colo., NCAR, 66 p.
- Logan, R. M., Derby, J. C., and Duncan, L. C., 1982, Acid precipitation and lake susceptibility in the central Washington Cascades: *Environmental Science & Technology*, v. 16, p. 771–775.
- McCull, J. G., 1981, Increasing hydrogen ion activity of water in two reservoirs supplying the San Francisco Bay area, California: *Water Resources Research*, v. 17, p. 1510–1516.
- Melack, J. M. Stoddard, J. L., and Dawson, D. R., 1983, Acid Precipitation and buffer capacity of lakes in the Sierra

- Nevada, California, in Hermann, R., and Johnson, A. I., eds., *Acid rain—a water resource issue for the 80's: American Water Resources Association International Symposium*, Denver, Colo., 1982, Proceedings, p. 35–41.
- Munger, J. W., and Eisenreich, S. J., 1983, Continental-scale variations in precipitation chemistry: *Environmental Science and Technology*, v. 17, p. 32A–42A.
- National Atmospheric Deposition Program, 1982, Distribution of surface waters sensitive to acidic precipitation: a state-level atlas. NADP Technical Report no. IV, Norton, S. A., ed., Department of Geological Sciences, Orono, University of Maine, 72 unnumbered pages.
- Norton, S. A., Davis, R. B., and Brakke, D. F., 1981, Responses of northern New England lakes to atmospheric inputs of acids and heavy metals—Completion report: Project A-048-ME, U.S. Department of the Interior, O.W.R.T., 90 p.
- Pearson, F. J., Jr., and Fisher, D. W., 1971, Chemical composition of atmospheric precipitation in the northeastern United States: U.S. Geological Survey Water-Supply Paper 1535-P, 23 p.
- Peters, N. E., Schroeder, R. A., and Troutman, D. E., 1982, Temporal trends in the acidity of precipitation and surface waters of New York: U.S. Geological Survey Water-Supply Paper 2188, 35 p.
- Pfeiffer, M. H., and Festa, P. J., 1980, Acidity status of lakes in the Adirondack region of New York in relation to fish resources: New York State Department of Environmental Conservation, FW-P168 (10/80), 36 p. and appendices.
- Rambo, D. L., and Karanas, J. J., 1982, An acid rain bibliography: Corvallis, Oreg., U.S. Environmental Protection Agency, CERL-053d, 2 v.
- Richter, D. D., Ralston, C. W., and Harms, W. R., 1983, Chemical composition and spatial variation of bulk precipitation at a coastal plain water-shed in South Carolina: *Water Resources Research*, v. 19, p. 134–140.
- Riley, S. J., ed., 1981, GEOREF thesaurus and guide to indexing: Falls Church, Va., American Geological Institute, 431 p.
- Ritter, J. R., and Brown, A. E., 1981, An evaluation of the effects of acid rain on low conductivity headwater streams in Pennsylvania: U.S. Geological Survey Open-File Report 81-1025, 53 p.
- Schofield, C. L., 1976, Acid precipitation—Effects on fish: *Ambio*, v. 5, no. 5–6, p. 228–230.
- Smith, R. A., and Alexander, R. B., 1983, Evidence for acid precipitation induced trends in common ion concentrations at Bench-Mark stations: U.S. Geological Survey Circular 910, 12 p.
- Stensland, G. J., 1980, Precipitation chemistry trends in the northeastern United States, in Toribara, T. Y., Miller, M. W., and Morrow, P. E., eds., 1980, *Polluted Rain*: New York, Plenum Press, p. 87–108.
- Stensland, G. J., and Semonin, R. G., 1982, Another interpretation of the pH trend in the United States: *Bulletin of the American Meteorological Society*, v. 63, p. 1277–1284.
- Summers, P. W., and Whelpdale, D. M., 1976, Acid precipitation in Canada: *Water, Air, and Soil Pollution*, v. 6, p. 447–455.
- United States–Canada Impact Assessment Working Group 1, 1983, Final (Phase III) report under U.S.–Canada Memorandum of Intent on Transboundary Air Pollution, 665 p.
- U.S. Environmental Protection Agency, 1983a, Total alkalinity of surface waters: Corvallis Environmental Research Laboratory, U.S. Environmental Protection Agency, Corvallis, Oreg., 6 p.
- 1983b, The acidic deposition phenomenon and its effects: *Critical Assessment Review Papers* (in press).
- U.S. Office of Water Research and Technology, 1980, *Water Resources Thesaurus* (3d ed.): Washington, D.C., U.S. Department of the Interior, v. 1, 72 p.; Descripto words, 36 p., Descriptors, 17 p.
- Watt, W. D., Scott, D., and Ray, S., 1979, Acidification and other chemical changes in Halifax County lakes after 21 years: *Limnology and Oceanography*, v. 24, p. 1154–1161.
- Wiltshire, D. A., and Evans, M. L., 1983, Acid precipitation—An annotated bibliography of the literature through 1981: U.S. Geological Survey Circular (in press).
- Wisniewski, Joseph, and Kinsman, J. D., 1982, An overview of acid rain monitoring activities in North America: *Bulletin of the American Meteorological Society*, v. 63, no. 6, p. 598–618.